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## ON CERTAIN SUBSTITUTED ACRYLIC AND PROPIONIC ACIDS.

BY CHARLES F. MABERY.

*Bromtrichlorpropionic Acid.*[1]— Chlorine unites readily with chlorbromacrylic acid, and when the reaction is conducted in a chloroform solution it is attended with the evolution of considerable heat. The best results are obtained, as regards both the purity and the yield of the addition-product, when the solution is kept cold and exposed to direct sunlight. In three or four hours the formation of the addition-product is complete, and upon evaporation of the chloroform it is left in the form of a crystalline solid that is easily purified by two or three crystallisations from carbonic disulphide. In one experiment, with the temperature at several degrees below zero, 6.5 grams chlorbromacrylic acid absorbed in two hours 1.5 grams chlorine, corresponding to an amount of bromtrichlorpropionic acid equivalent to ninety per cent. of the theoretical yield.

In its general character and crystalline form this acid resembles the other substituted acids of this series. It is somewhat soluble in water, with small quantities of which it forms an oil readily soluble in ether, alcohol and chloroform. From a hot solution in

[1] In the preparation and study of bromtrichlorpropionic and trichloracrylic acids I have been successively aided by the late Mr. Wallace J. Meyer and Mr. Perry L. Hobbs, formerly students in this laboratory.

carbonic disulphide it separates on cooling in rhombic prisms, which melt at 83°-84°. It decomposes carbonates readily in the cold, with the formation of the corresponding salts, while alkaline hydrates eliminate the elements of hydrobromic acid. The salts of this acid are comparatively unstable; they are rapidly decomposed when heated, and the silver salt suffers decomposition at ordinary temperatures. The identity of the acid was established by analysis and a study of several of its salts.

I. 0.4204 gram of the substance gave 0.2201 gram $CO_2$ and 0.0330 gram $H_2O$.

II. 0.2540 gram of the substance gave 0.5005 gram AgCl+AgBr.

| | Calculated for $C_3H_2Cl_3BrO_2$. | Found. I. | II. |
|---|---|---|---|
| C | 14.04 | 14.28 | ... |
| H | .78 | .87 | ... |
| 3Cl+Br | 72.71 | ... | 72.57 |

The following salts were prepared for analysis:

*Baric Bromtrichlorpropionate*, $Ba(C_3Cl_3BrO_2H)_2$.—At ordinary temperatures the barium salt appears to be perfectly stable, and it may be obtained by neutralising a solution of the acid with baric carbonate and baric hydrate and allowing it to evaporate spontaneously without the application of heat. It is very soluble in water, and it is left upon evaporation as a gummy mass, which becomes solid on standing. The air-dried salt lost nothing in weight over sulphuric acid, although it was rapidly decomposed when heated to 80°.

0.8894 gram of the salt dried over $H_2SO_4$ gave 0.3220 gram $BaSO_4$.

| | Calculated for $Ba(C_3Cl_3BrO_2H)_2$. | Found. |
|---|---|---|
| Ba | 21.28 | 21.13 |

*Calcic Bromtrichlorpropionate*, $Ca(C_3Cl_3BrO_2H)_2$.—The calcium salt may be prepared at ordinary temperatures by neutralisation of the acid with calcic carbonate and calcic hydrate. Upon evaporation the salt was deposited in oblique prisms, which were constant in weight over sulphuric acid after drying in the air.

I. 0.6096 gram of the salt dried over $H_2SO_4$ gave 0.1522 gram $CaSO_4$.

II. 0.5792 gram of the salt gave 0.1426 gram $CaSO_4$.

| | Calculated for $Ca(C_3Cl_3BrO_2H)_2$. | Found. I. | II. |
|---|---|---|---|
| Ca | 7.30 | 7.35 | 7.24 |

*Potassic Bromtrichlorpropionate*, $KC_3Cl_3BrO_2H.2H_2O$.—A neutral solution of the potassium salt may be evaporated at ordinary temperatures without decomposition. From the concentrated solution the salt separates in rhombic plates that are quite soluble in water and easily decomposed by heat. For analysis a constant weight of the air-dried salt was obtained over sulphuric acid.

I. 1.0927 of the air-dried salt lost over $H_2SO_4$, 0.1142 gram $H_2O$.

II. 0.7857 of the air-dried salt lost over $H_2SO_4$, 0.0805 gram $H_2O$.

III. 0.6986 gram of the anhydrous salt gave 0.2116 gram $K_2SO_4$.

| | Calculated for $KC_3Cl_3BrO_2H_2.2H_2O$. | Found. I. | II. |
|---|---|---|---|
| $H_2O$ | 10.89 | 10.46 | 10.26 |

| | Calculated for $KC_3Cl_3BrO_2H$. | Found. |
|---|---|---|
| K | 13.27 | 13.59 |

*Trichloracrylic Acid.*— Trichloracrylic acid is prepared from bromtrichlorpropionic acid by the action of baric hydrate most conveniently, taking a slight excess over the calculated amount and keeping the solution slightly alkaline for one or two days. Upon acidifying the solution with hydrochloric acid and extracting with ether, the acid is left after evaporation of the ether as an oily liquid which soon solidifies. The crude acid is easily purified by crystallisation from carbonic disulphide, in which it is much less soluble cold than hot. It is sparingly soluble in water, with which it forms an oil, and very soluble in alcohol, ether and chloroform. From carbonic disulphide the acid crystallises in rhombic prisms, which resemble closely the forms of tribromacrylic acid. Its melting-point is 76°. The composition of this acid was established by the following analyses:

I. 0.1942 gram of the substance gave, by Carius' method, 0.4783 gram AgCl.

II. 0.3182 gram of the substance gave 0.2362 gram $CO_2$ and 0.1068 gram $H_2O$.

| | Calculated for $C_3HCl_3O_2$. | Found. I. | II. |
|---|---|---|---|
| Cl | 60.70 | 60.75 | ... |
| C | 20.51 | ... | 20.24 |
| H | .58 | ... | .37 |

The solubility of trichloracrylic acid in cold water was deter-

mined by the method of V. Meyer. After neutralising the saturated solution with baric carbonate and evaporating to dryness, the barium was determined by ignition with sulphuric acid.

I. 3.8442 grams of a solution saturated at 20° gave 0.1580 gram $BaSO_4$.

II. 4.4664 grams of a solution saturated at 20° gave 0.1738 gram $BaSO_4$.

These determinations correspond to the following percentages:

| I. | II. |
|---|---|
| 6.19 | 5.86 |

*Baric Trichloracrylate*, $Ba(C_3Cl_3O_2)_2\ 3\frac{1}{2}H_2O$.—A solution of the barium salt prepared by neutralising the acid with baric carbonate, may be evaporated on the steam-bath without decomposition, and the salt separates from a concentrated solution in the form of branching needles with pearly lustre, which are much less soluble in cold than in hot water. The air-dried salt contains three and a half molecules of water, which are given up at 80°.

I. 1.1638 grams of the air-dried salt lost 0.1338 gram $H_2O$ at 80°.

II. 1.2335 grams of the air-dried salt lost 0.1383 gram $H_2O$ at 80°.

III. 0.6194 gram of the air-dried salt lost 0.0686 gram $H_2O$ at 80°.

IV. 1.4194 grams of the air-dried salt lost 0.1582 gram $H_2O$ at 80°.

V. 0.6044 gram of the anhydrous salt gave, by ignition with $H_2SO_4$, 0.2916 gram $BaSO_4$.

VI. 0.4980 gram of the anhydrous salt gave 0.2372 gram $BaSO_4$.

VII. 0.9452 gram of the anhydrous salt gave 0.4460 gram $BaSO_4$.

| | Calculated for $Ba(C_3Cl_3O_2)_2\ 3\frac{1}{2}H_2O$. | Found. I. | II. | III. | IV. |
|---|---|---|---|---|---|
| $H_2O$ | 11.48 | 11.53 | 11.22 | 11.08 | 11.14 |

| | Calculated for $Ba(C_3Cl_3O_2)_2$. | Found. V. | VI. | VII. |
|---|---|---|---|---|
| Ba | 28.19 | 28.36 | 28.00 | 27.74 |

*Calcic Trichloracrylate*, $Ca(C_3Cl_3O_2)_2\ 3\frac{1}{2}H_2O$.—The calcium salt resembles the barium salt in its solubility in water, although it appears to be somewhat more soluble in the cold. It separates from a concentrated hot solution on cooling in tufts of branching

needles. For analysis, the air-dried salt was heated to a constant weight at 80°.

I. 0.6220 gram of the air-dried salt lost 0.0854 gram $H_2O$ at 80°.

II. 0.6000 gram of the air-dried salt lost 0.0807 gram $H_2O$ at 80°.

III. 0.9238 gram of the air-dried salt lost 0.1279 gram $H_2O$ at 80°.

IV. 0.5026 gram of the anhydrous salt gave 0.1692 gram $CaSO_4$.

| | Calculated for $Ca(C_3Cl_3O_2)_2{\cdot}\frac{1}{2}H_2O$. | Found. I. | II. | III. |
|---|---|---|---|---|
| $H_2O$ | 13.94 | 13.73 | 13.45 | 13.85 |

| | Calculated for $Ca(C_3Cl_3O_2)_2$. | Found. |
|---|---|---|
| Ca | 10.26 | 9.90 |

*Potassic Trichloracrylate*, $KC_3Cl_3O_2$.—A neutral solution of the potassium salt when concentrated on the steam-bath deposits the salt in the form of irregular plates, which are sparingly soluble in cold water, very soluble in hot. It cannot be heated to 80° without decomposition, and it loses nothing in weight over sulphuric acid after drying by exposure to the air.

1.0159 grams of salt dried over sulphuric acid gave 0.4209 gram $K_2SO_4$.

| | Calculated for $KC_3Cl_3O_2$. | Found. |
|---|---|---|
| K | 18.60 | 18.31 |

*Argentic Trichloracrylate*, $AgC_3Cl_3O_2$.—The silver salt may be made by the addition of argentic nitrate to an aqueous solution of the acid. It is precipitated in fine felted needles, which are very sparingly soluble in cold water, more soluble in hot, and it may be recrystallised from a hot solution without decomposition.

0.6002 gram of the salt gave 0.3020 gram AgCl.

| | Calculated for $AgC_3Cl_3O_2$. | Found. |
|---|---|---|
| Ag | 38.23 | 37.90 |

In a former paper[1] on certain tetrasubstituted propionic acids, by H. B. Hill and myself, it was shown that the addition-product that resulted from the action of chlorine on $\alpha$-dibromacrylic acid was essentially different in its properties from the product obtained by the addition of bromine to $\alpha$-dibromacrylic acid. Since there seems to be little doubt that the positions of the halogens in dibrom- and dichloracrylic acids are represented by the formula CXH=

[1] This Journal **3**, 263.

CX — COOH, the addition-products of these acids should be identical. It therefore seemed advisable to seek further confirmation of the results described in the above-mentioned paper in a comparison of the products which I found could be obtained by elimination of the elements of hydrobromic acid from these tetrasubstituted propionic acids. This work was carried on with the assistance of Mr. Perry L. Hobbs.

*Bromdichloracrylic Acid from α-Dibromdichlorpropionic Acid.* The preparation of α-dibromdichlorpropionic acid from dichloracrylic by the addition of bromine was fully described in the paper cited above. When this acid in aqueous solution is treated with baric hydrate in quantity sufficient to complete the reaction $2C_3Br_2Cl_2O_4H_2 + BaO_2H_2 = 2C_3BrCl_2O_2H + BaBr_2 + 2H_2O$, the solution retains its acid character until nearly the calculated amount is added. But since the product, if immediately extracted, proves to contain unaltered dibromdichlorpropionic acid, which renders its purification somewhat difficult, it is better to keep the solution slightly alkaline for twenty-four hours. It may then be acidified, the oil that separates allowed to subside, and the solution extracted with ether. The product is easily purified by crystallisation from carbonic disulphide or from water, since either of these solvents dissolves it more freely hot than cold. This acid is readily soluble in alcohol and ether; less soluble in chloroform and carbonic disulphide. When heated with water it melts before dissolving, but solidifies on cooling. By slow evaporation of an aqueous solution the acid separates in oblique prisms, which melt at 85°. Its composition was determined by analysis.

I. 0.2150 gram of the substance gave 0.4661 gram AgCl+AgBr.

II. 0.7352 gram of the substance gave 0.4465 gram $CO_2$ and 0.0424 gram $H_2O$.

III. 0.6420 gram of the substance gave 0.3842 gram $CO_2$ and 0.0775 gram $H_2O$.

| | Calculated for $C_3BrCl_2O_2H$. | Found. I. | II. | III. |
|---|---|---|---|---|
| 2Cl+Br | 68.64 | 68.93 | ... | ... |
| C | 16.36 | ... | 16.56 | 16.32 |
| H | .46 | ... | .64 | 1.27 |

In determining the solubility of this acid in cold water, a solution was made according to the method of V. Meyer, saturated

with baric carbonate, and the barium determined by ignition with sulphuric acid.

I. 3.7883 grams of a solution saturated at 20° gave 0.1030 gram $BaSO_4$.

II. 3.5945 grams of a solution saturated at 20° gave 0.1001 gram $BaSO_4$.

These results correspond to the following percentages:

| I. | II. |
|---|---|
| 2.56 | 2.62 |

*Baric Bromdichloracrylate*, $Ba(C_3BrCl_2O_2)_2 3H_2O$.—Upon evaporation of a solution of this salt, prepared by neutralising the acid with baric carbonate, the salt was deposited in rhombic plates, which were much less soluble in cold than in hot water. When dried to a constant weight in the air it lost three molecules of water at 80°.

I. 0.9585 gram of the air-dried salt lost 0.9210 gram $H_2O$ at 80°.

II. 0.9346 gram of the air-dried salt lost 0.9220 gram $H_2O$ at 80°.

| | Calculated for $Ba(C_3BrCl_2O_2)_2 3H_2O$. | Found. I. | Found. II. |
|---|---|---|---|
| $H_2O$ | 8.58 | 8.34 | 8.36 |

| | Calculated for $Ba(C_3BrCl_2O_2)_2$. | Found. |
|---|---|---|
| Ba | 23.82 | 23.51 |

*Calcic Bromdichloracrylate*, $Ca(C_3BrCl_2O_2)_2 4H_2O$.—This salt was deposited from a concentrated solution in jagged plates, which were quite soluble in water. After drying by exposure to the air, the salt lost four molecules of water when heated to 80°.

I. 0.8334 gram of the air-dried salt lost 0.1054 gram $H_2O$ at 80°.

II. 0.8027 gram of the air-dried salt lost 0.1014 gram $H_2O$ at 80°.

III. 0.7556 gram of the anhydrous salt gave 0.2150 gram $CaSO_4$.

| | Calculated for $Ca(C_3BrCl_2O_2)_2 4H_2O$. | Found. I. | Found. II. |
|---|---|---|---|
| $H_2O$ | 13.09 | 12.54 | 12.63 |

| | Calculated for $Ca(C_3BrCl_2O_2)_2$. | Found. |
|---|---|---|
| Ca | 8.37 | 8.32 |

*Potassic Bromdichloracrylate*, $KC_3BrCl_2O_2$.—When deposited from a hot solution the potassium salt forms clusters of anhydrous, pearly needles, which are not decomposed when heated to 80°.

1.0234 grams of the salt dried at 80° gave 0.3565 gram $K_2SO_4$.

| | Calculated for $KC_3BrCl_2O_2$. | Found. |
|---|---|---|
| K | 15.15 | 15.63 |

*Argentic Bromdichloracrylate*, $AgC_3BrCl_2O_2$.—Upon the addition of argentic nitrate to an aqueous solution of the acid, the silver salt forms a bulky precipitate, which is composed of fine needles. The salt is much less soluble in cold than in hot water, and it may be crystallised from a hot solution without decomposition. It is not readily decomposed by the action of light.

0.9247 gram of the salt gave 0.4091 gram AgCl.

| | Calculated for $AgC_3BrCl_2O_2$. | Found. |
|---|---|---|
| Ag | 33.03 | 33.31 |

*Bromdichloracrylic Acid from β-Dibromdichlorpropionic Acid.* In the formation of β-dibromdichlorpropionic acid from αβ-dibromacrylic, it was found by H. B. Hill and me that, under proper conditions, the addition of chlorine was easily accomplished, and there seemed little probability of a molecular rearrangement during the progress of the reaction. Recent results confirm this conclusion, especially at low temperatures. In one experiment in direct sunlight, with the temperature at —5°, twenty grams dibromacrylic acid absorbed sufficient chlorine in about one hour to form nearly the theoretical amount of the addition-product. The elements of hydrobromic acid are easily abstracted from this acid by baric hydrate, and when the reaction is conducted in a slightly alkaline solution, it is usually complete in twenty-four hours. Upon acidifying the solution, the product in part falls as an oil, and the remainder may be extracted with ether. Evaporation of the ether leaves an oil which solidifies on standing, and it may be easily purified by successive crystallisations from carbonic disulphide. The acid is sparingly soluble in cold carbonic disulphide and chloroform, readily soluble in alcohol and ether. With water it forms an oil that does not solidify at 0°. It melts at 78°–80°, and forms oblique prisms when deposited slowly from a saturated solution in carbonic disulphide. Its composition was shown by the following analyses:

I. 0.2700 gram of the substance gave 0.5828 gram AgCl + AgBr.

II. 0.2099 gram of the substance gave 0.4490 gram AgCl + AgBr.

III. 0.8560 gram of the substance gave 0.5072 gram $CO_2$ and 0.0973 gram $H_2O$.

| | Calculated for $C_3BrCl_2O_2H$. | Found. I. | II. | III. |
|---|---|---|---|---|
| Br + 2Cl | 68.64 | 68.61 | 68.00 | ... |
| C | 16.36 | ... | ... | 16.15 |
| H | .46 | ... | ... | 1.00 |

The solubility of the acid in cold water was determined by neutralising a saturated solution with baric carbonate, and determining the barium by ignition with sulphuric acid.

I. 3.2754 grams of a solution saturated at 20° gave 0.1206 gram $BaSO_4$.

II. 4.8832 grams of a solution saturated at 20° gave 0.1793 gram $BaSO_4$.

These results correspond to the percentages:

| I. | II. |
|---|---|
| 6.92 | 6.90 |

*Baric Bromdichloracrylate*, $Ba(C_3BrCl_2O_2)_2\,3H_2O$. — From a saturated hot solution prepared by neutralising the acid with baric carbonate and evaporating, the barium salt separates in rhombic plates, which are more soluble in hot than in cold water.

I. 0.9841 gram of the air-dried salt lost 0.0854 gram $H_2O$ at 80°.

II. 1.1431 grams of the air-dried salt lost 0.0998 gram $H_2O$ at 80°.

III. 0.7350 gram of the air-dried salt lost 0.0649 gram $H_2O$ at 80°.

IV. 0.9226 gram of the anhydrous salt gave 0.3778 gram $BaSO_4$.

V. 0.9650 gram of the anhydrous salt gave 0.3982 gram $BaSO_4$.

| | Calculated for $Ba(C_3BrCl_2O_2)_2\,3H_2O$. | Found. I. | II. | III. |
|---|---|---|---|---|
| $H_2O$ | 8.58 | 8.68 | 8.71 | 8.83 |

| | Calculated for $Ba(C_3BrCl_2O_2)_2$. | Found. IV. | V. |
|---|---|---|---|
| Ba | 23.82 | 24.14 | 24.26 |

*Calcic Bromdichloracrylate*, $Ca(C_3BrCl_2O_2)_2\,4H_2O$.—The calcium salt crystallises from a hot saturated solution in pearly branching needles, which contain four molecules of crystal water when dried in the air.

I. 0.8742 gram of the air-dried salt lost 0.1134 gram $H_2O$ at 80°.

II. 0.5368 gram of the air-dried salt lost 0.1824 gram $H_2O$ at 80°.

III. 0.5368 gram of the anhydrous salt gave 0.1606 gram $CaSO_4$.

| | Calculated for $Ca(C_3BrCl_2O_2)_2 4H_2O$. | Found. I. | Found. II. |
|---|---|---|---|
| $H_2O$ | 13.09 | 12.97 | 13.32 |
| | Calculated for $Ca(C_3BrCl_2O)_2$. | Found. | |
| Ca | 8.38 | 8.79 | |

*Potassic Bromdichloracrylate*, $KC_3BrCl_2O_2$.—The potassium salt is made by neutralising the acid with potassic carbonate, and it is deposited from a concentrated hot solution in clusters of fine needles which are not decomposed at 80°.

0.7714 gram of the salt dried over $H_2SO_4$ gave 0.2662 gram $K_2SO_4$.

| | Calculated for $KC_3BrCl_2O_2$. | Found. |
|---|---|---|
| K | 15.15 | 15.49 |

*Argentic Bromdichloracrylate*, $AgC_3BrCl_2O_2$.—The silver salt is precipitated in masses of fine needles upon the addition of argentic nitrate to a solution of the acid. It may be recrystallised without decomposition from hot water, in which it is freely soluble, and it is not appreciably affected when exposed to the action of light.

I. 0.9945 gram of the salt gave 0.4411 gram AgCl.

II. 0.8611 gram of the salt gave 0.3780 gram AgCl.

| | Calculated for $AgC_3BrCl_2O_2$. | Found. I. | Found. II. |
|---|---|---|---|
| Ag | 33.03 | 33.62 | 33.05 |

From the results of this examination, it seems that while the salts of these acids present certain similarities in the water of crystallisation, the physical properties of the acids themselves are essentially different. The explanation offered by Beilstein, in the last edition of the Handbuch der organischen Chemie, to account for the difference in properties of $\alpha$- and $\beta$-dibromdichloracrylic acids by assigning to dibrom- and dichloracrylic acids the formula $CX_2{=}CH-COOH$, is theoretically satisfactory; but, unfortunately, it is not supported by experimental evidence thus far obtained, which has been fully reviewed.[1] Although the replacement of an atom of bromine by one of chlorine during the addition of chlorine to $\alpha\beta$-dibromacrylic acid seems improbable, it can hardly be regarded as impossible. The replaced atom of bromine would be taken up immediately by chlorine, and the resulting chlorine monobromide might form an addition-product even more readily than chlorine

[1] H. B. Hill, this Journal **4**, 273.

itself. These reactions might give a substituted acrylic acid with the formula $CCl_2 = CBr - COOH$, which is the only form theoretically possible with a structure different from that of the corresponding product given by $\alpha\beta$-dichloracrylic acid.

CASE SCHOOL OF APPLIED SCIENCE, *October* 26, 1886.

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## ON THE COMPOSITION OF CERTAIN PRODUCTS FROM THE COWLES ELECTRICAL FURNACE.

BY CHARLES F. MABERY.

In a paper presented by the Messrs. Cowles and the writer at the meeting of the American Association for the Advancement of Science at Ann Arbor in 1885, an account was given of the application of electricity to the reduction of refractory oxides, and certain products were described which had been taken from the electrical furnace. At the recent meeting of the association at Buffalo, a paper was presented by myself which gave a description of material that had been obtained during the past year. In this paper I propose to give a more precise account of some of these products, together with analytical results which establish their composition.

### *Reduction of Aluminum from Corundum.*

When corundum, mixed with charcoal, is submitted to the action of an electrical current in this furnace, it is immediately fused and reduction of the molten mass proceeds rapidly. The reduced metal is converted into vapor, which in part condenses in the upper layer of charcoal, while no inconsiderable portion is carried out of the furnace by the escaping gases and burns in the air. Analyses of the mixture of carbon and metal where condensation takes place have shown from ten to fifty per cent. of metallic aluminum. Soot collected at the orifices for the escape of the gaseous products usually contains metallic aluminum, sometimes to the extent of ten or twelve per cent. of its weight. If the ore contains silica the reduced silicon unites with the aluminum in variable proportions below ten per cent. of silicon. A similar reduction takes place with clay; the silicon is dissolved in the metallic aluminum

while in the molten state, and solution of the latter in hydrochloric acid leaves the silicon in the crystalline or graphitic form. The greater portion of the aluminum, however, may be retained within the furnace by conducting the reduction in presence of a metal with a higher specific gravity, such as copper, iron or tin. If copper is added to the charge of ore, it unites with the reduced aluminum in variable proportions, which depend upon the conditions of the experiment. The approximate composition of this alloy can be closely estimated by inspection as it is taken from the furnace. Ten per cent. of aluminum forms the well-known bronze, which is malleable, golden yellow in color, and quite hard. An increase of two or three per cent. of aluminum forms an extremely hard, brittle alloy. A fifteen per cent. product has a shiny lustre, a steel-gray color, and it may easily be reduced to the finest powder. As the percentage of aluminum increases, the product becomes less lustrous and lighter in color.

The composition of the slag that accompanies the reduction of aluminum is somewhat variable. It usually contains calcic aluminate, which is formed from the lime with which the charcoal is treated previous to use. When first taken from the furnace it is hard and compact, but upon exposure to the air it soon falls to a fine powder which shows an alkaline reaction. It is always found above the alloy in the furnace, and it is usually free from copper or alloy. Occasionally, when fused corundum is the chief constituent, it has a fine granular structure; otherwise it presents a crystalline structure, with a shiny vitreous lustre. The following analyses represent the composition of several slags from experiments made under different conditions:

| | I. | II. | III. | IV. | V. | VI. |
|---|---|---|---|---|---|---|
| $Al_2O_3$ (insoluble) | 55.3 | 66.84 | ... | 69 | ... | ... |
| $Al_2O_3$ (soluble)$+Al_2\left(\frac{\text{calc.}}{\text{as } Al_2}\right)$ | 21.8 | 14.2 | 26.9 | 11.8 | ... | ... |
| CaO | 3.7 | 1.44 | ... | 6.77 | ... | ... |
| Cu | ... | 3.32 | ... | 1.00 | ... | ... |
| C (total) | ... | ... | ... | .69 | .65 | ... |
| C (combined) | ... | ... | .8 | ... | ... | .7 |

These slags usually contain metallic aluminum, as shown by evolution of hydrogen with hydrochloric acid or alkaline hydrates. They rarely contain iron, and are usually nearly free from silicon. The percentage of carbon, as given by direct combustion, or by evolution as a hydrocarbon with dilute acids, has not differed

materially from the results in analyses 3, 4, 5 and 6, given above. Since in the products analysed iron was absent, it would seem that the carbon might be present in the form of a carbide of aluminum.[1]

The reduced metals frequently alloy in proportions that form peculiar products. They sometimes show a crystalline structure, are variable in color, between steel-gray and bright yellow, often with a resinous lustre, and semi-transparent. These alloys contain aluminum, copper, silicon and calcium in variable proportions, and upon exposure to the air they fall to a powder. At 100° they decompose water, with the evolution of hydrogen, and impart an alkaline reaction to the solution, probably due to the presence of metallic calcium.[2] Products similar in appearance are formed when tin instead of copper is mixed with the charge of ore. The following results were obtained in analysis of some of these alloys:

| | I. | II. | III. | IV. |
|---|---|---|---|---|
| Cu | 26.7 | 35 | 20.00 | ... |
| $Al_2$ | 66.2 | 53.3 | 74.32 | 15.23 |
| Si | 5 | 12.3 | 2.86 | 20.55 |
| Ca | 2 | .2 | 2.86 | ... |
| Sn | ... | ... | ... | 49.26 |

Upon dissolving the alloy in acids, the silicon was left as a crystalline residue, which was converted into the dioxide by fusion with alkaline carbonates and potassic nitrate. In nearly all specimens of this product the presence of nitrogen could be detected by fusion with potassic hydrate, although several quantitative determinations showed only a small fraction of one per cent. of this element.

### *Reduction of Corundum in Presence of Iron.*

Although iron does not ordinarily form alloys with as high a percentage of aluminum as copper, it will retain aluminum to a greater or less extent. A product obtained by smelting corundum with iron has recently attracted considerable attention. It seems to possess valuable properties for foundry purposes, and it is also available for introducing a small percentage of aluminum into

[1] Various mixtures of aluminum and carbon, as well as the crystalline alloys described above, were first thought to be carbides of aluminum (see Am. Journ. of Science **30**, 310); and it is probable that this compound is formed in limited quantities when the reduction of aluminum is conducted in the absence of other metals.

[2] Before exposure to the air these alloys gave no alkaline reaction with water at ordinary temperatures. Wöhler (Journ. pract. Chemie [2] **26**, 385 and 474) found that an alloy of calcium and aluminum containing 8 per cent. calcium was permanent in air and water.

steel. When taken from the electrical furnace it presents the appearance of a very hard, fine-grained white iron, and it contains usually six to ten per cent. of aluminum. Analyses of different ingots gave the following results:

| | I. | II. | III. | IV. | V. |
|---|---|---|---|---|---|
| Fe | 85.17 | 85.46 | 86.04 | 86 | 84.0 |
| $Al_2$ | 8.02 | 8.65 | 9 | 9.25 | 10 5 |
| Si | 2.36 | 2.20 | 2.52 | 2.35 | 2.4 |
| C | ... | 3.77 | ... | 2.41 | 2.5 |

The composition of the slag that is formed with the alloy of aluminum and iron is shown by the following analyses:

| | I. | II. |
|---|---|---|
| $SiO_2$ | 0.78 | 4.1 |
| $Al_2O_3$ (insoluble) | 0.20 | ... |
| CaO | 28.5 | 14.0 |
| Fe | 1.5 | 29.16 |
| $Al_2 + Al_2O_3$ [sol.] (calc. as $Al_2$) | 38 | 48.70 |
| S | 0.5 | ... |
| Graphite | 5.0 | 2.60 |
| Combined C | 0.9 | 0.48 |

*Reduction of Silica.*

Sand is reduced in the electrical furnace more readily than corundum. The oxide is first melted, and large masses of fused quartz may be taken from the furnace if the process is suspended at the proper stage. Reduction follows immediately after fusion, and, upon cooling, the reduced silicon assumes the crystalline condition. If copper is mixed with the charge of ore, it dissolves the silicon in variable proportions below fourteen per cent., which is the largest amount that has been observed. The addition of a small percentage of silicon to certain metals produces a marked increase in their tensile strength. Silicon bronze shows greater strength than copper, tin bronze, or phosphor bronze. The greatest strength hitherto assigned to ten per cent. aluminum bronze is 100,000 pounds per square inch; by the addition of one or two per cent. of silicon the strength of this alloy is frequently increased to 120,000 pounds.

*Silicon Monoxide.*

The product obtained by reduction of silica in the absence of

metals is usually composed to a greater or less extent of an amorphous substance, greenish yellow, occasionally inclining to deep green in color, with a vitreous lustre. Since it is always found between the unreduced oxide and silicon, its formation would seem to be the result of partial reduction. This inference is confirmed by analysis, although as yet it has been possible to obtain only a small quantity of pure substance, as indicated by the following results:

I. 0.6319 gram of the substance gave 0.8357 gram $SiO_2$.

II. 0.4225 gram of the substance gave 0.5611 gram $SiO_2$.

III. 0.4523 gram of the substance gave 0.6198 gram $SiO_2$.

| Calculated for SiO. | Found. | | |
|---|---|---|---|
| | I. | II. | III. |
| 100 | 96.45 | 98.60 | 99.88 |

This substance is attacked by hydrofluoric acid, although apparently less readily than the dioxide. In specimens containing reduced silicon the latter was left untouched after treatment with this acid. The samples selected for analysis left no residue when treated with hydrofluoric acid. It is slowly changed to the dioxide by fusion with a mixture of alkaline carbonates and potassic nitrate, and it was by this method that the results given above were obtained. One determination of its specific gravity gave 2.893 with water at 4°. This value is somewhat higher than the specific gravity of quartz, 2.6–2.66 (Graham, Alte ausführliches Lehrbuch der Chemie). From the method of its formation, the results of analysis, and the properties of this substance, there seems to be little doubt that it is silicon monoxide.

In the analysis of these products I have received valuable aid from my assistants, Messrs. H. L. Paine, A. W. Smith, C. H. Matthiessen, and from Mr. H. N. Yates, analytical chemist to the Cowles Electric Smelting and Aluminum Company.

Contributions from the Chemical Laboratory U. S. Department of Agriculture.

## IX.—AMERICAN BARLEY.

By Clifford Richardson.

Notwithstanding the importance to the brewing interests of this country of an accurate knowledge of the characteristics of our barleys, but few analyses have been made hitherto. These include nine collected by Brewer in his Report to the Tenth Census, and eleven specimens examined at the Brewers' Experiment Station, New York. Abroad more attention has been paid to the subject, especially by Maercker[1] at Halle, who concludes that the production of barley cannot be improved by selection of seed alone. Care in other directions and favorable climatic influences, over which there is no control, are necessary as well. Heavy manuring with nitrogen is most injurious, increasing the albuminoids; and a barley rich in these constituents he has found, from experience, to be poor in quality, while a low content is, as a rule, expressive of high quality, the effects of rain and moisture being excluded. From the weight per bushel but little can be learned, and he decides that little attention should be paid to it. The mealiness of the grain was found, however, to be a most important indication, glassy grain being too rich in albuminoids. In fact, as a whole, the characteristics of a good barley are fine color, mealy consistency and small amount of albuminoids. Accordingly, he grades as follows the crops raised at Halle from certain selected seed which had been cultivated with the intention of improving the grain grown in that vicinity:

| Specimens denominated. | Mean percent. of albuminoids. |
|---|---|
| Extremely fine, | 8.09 |
| Fine, | 8.67 |
| Good, | 8.93 |
| Medium, | 9.78 |
| Under medium, | 10.24 |

and finds the mealiness of the crop as compared to that of the seed to be, under different conditions of nitrogenous manuring:

[1] Magdeburgische Zeitung, 1885, 443 and 445; Bied. Centbl. f. Agrikulturchemie **13**, 491-9.

| | Per Cent. of Mealy Kernels. | | | |
|---|---|---|---|---|
| | Saalish. | Danish. | Moravian. | Slavonian. |
| Seed, . . . . . | 80.0 per ct. | 90.0 per ct. | 90.0 per ct. | 92.0 per ct. |
| 100 kilograms saltpetre, | 62.4 | 70.1 | 68.7 | 77.5 |
| 200 kilograms saltpetre, | 64.9 | 65.9 | 66.8 | 64.7 |
| Mean, . . . . . | 63.7 | 68.0 | 67.8 | 71.1 |
| Less than seed, . . . | 16.3 | 22.0 | 22.2 | 20.9 |

These results are of interest, and, aside from a knowledge of the percentage of albuminoids in barleys from various sources on the Continent and elsewhere, form the only basis which we have for a study of the character and relative value of this grain, as it is grown in different parts of this country, and matured under the most varied conditions of climate and general environment.

The samples of American barley have been collected from those parts of the country where it is a crop of any prominence. They represent fairly well the production of the United States and Canada, although the harvest in Canada was not quite equal to the average. The largest number of analyses are not for the largest areas of production—New York, Wisconsin and California, which raise more than half the crop—but they are scattered through all the States where any amount of barley is grown. In considering the average features of this cereal as it is found in market, regard must be had especially for the figures for Canada and the three States named, although the California barley reaches our Eastern markets in small amount.

Omitting the analyses in detail, which can be found in our original bulletin, the following are the averages derived from them:

*Average Physical Properties of American Barleys.*

| State. | No. of determinations. | Weight per 100 grains. | Weight per bushel. | Mealy. | Half mealy | Quarter mealy | Little mealy | Glassy. |
|---|---|---|---|---|---|---|---|---|
| | | Grams. | Pounds. | | | | | |
| United States..... | 76 | 3.482 | 54.0 | 20 | 35 | 29 | 15 | 1 |
| Canada..... | 12 | 3.088 | 54.1 | 19 | 37 | 29 | 13 | 2 |
| Eastern States..... | 13 | 3.016 | 52.6 | 11 | 29 | 32 | 26 | 2 |
| Western States..... | 39 | 3.171 | 52.8 | 21 | 35 | 30 | 13 | 1 |
| Northwestern States..... | 10 | 3.680 | 57.2 | 27 | 35 | 26 | 11 | 1 |
| Pacific Slope..... | 12 | 4.655 | 56.8 | 21 | 40 | 29 | 10 | 0 |
| Vermont..... | 3 | 3.193 | 52.0 | 13 | 24 | 34 | 24 | 5 |
| New York..... | 8 | 3.217 | 53.1 | 11 | 34 | 31 | 26 | 0 |
| Ohio..... | 4 | 3.230 | 52.1 | 33 | 38 | 21 | 8 | 0 |
| Michigan..... | 6 | 3.150 | 54.0 | 14 | 34 | 34 | 16 | 1 |
| Indiana..... | 3 | 3.330 | 53.5 | 28 | 35 | 24 | 13 | 0 |
| Illinois..... | 5 | 2.890 | 51.1 | 28 | 32 | 25 | 15 | 0 |
| Wisconsin..... | 5 | 3.320 | 51.3 | 22 | 30 | 31 | 14 | 3 |
| Minnesota..... | 7 | 3.290 | 52.7 | 22 | 43 | 29 | 6 | 0 |
| Iowa..... | 7 | 3.030 | 53.4 | 17 | 34 | 32 | 16 | 1 |
| Dakota..... | 5 | 3.354 | 54.2 | 15 | 39 | 32 | 13 | 1 |
| Montana..... | 5 | 4.220 | 59.1 | 45 | 28 | 17 | 10 | 0 |
| Nevada..... | 2 | 4.215 | 55.7 | .... | .... | .... | .... | 0 |
| Oregon..... | 2 | 4.800 | 56.1 | 12 | 30 | 40 | 18 | 0 |
| California..... | 5 | 4.900 | 53.0 | 26 | 46 | 23 | 5 | 0 |

*Average Composition of American Barleys (Unhulled) Arranged by States.*

| State. | Number of analyses. | Water. | Ash. | Oil. | Carbhydrates | Fibre. | Albuminoids. | Nitrogen. |
|---|---|---|---|---|---|---|---|---|
| | | Per ct | Per ct | Per ct | Per ct | Per ct | Per ct | Per ct |
| United States | 60 | 6.53 | 2.89 | 2.68 | 72.77 | 3.80 | 11.33 | 1.81 |
| Atlantic Slope | 10 | 6.64 | 2.51 | 2.59 | 73.02 | 3.57 | 11.59 | 1.85 |
| Northern States | 48 | 6.55 | 2.87 | 2.69 | 72.55 | 3.76 | 11.58 | 1.85 |
| Western States | 30 | 6.66 | 2.96 | 2.73 | 72.26 | 3.87 | 11.52 | 1.84 |
| Northwestern States | 8 | 6.62 | 2.85 | 2.69 | 73.03 | 3.59 | 11.82 | 1.89 |
| Pacific Slope | 10 | 6.47 | 3.05 | 2.63 | 72.43 | 3.90 | 11.50 | 1.69 |
| Vermont | 3 | 6.58 | 2.51 | 2.77 | 71.41 | 3.84 | 12.89 | 2.06 |
| Connecticut | 1 | 6.50 | 2.99 | 2.33 | 75.14 | 2.89 | 10.15 | 1.62 |
| New York | 5 | 6.77 | 2.46 | 2.65 | 73.59 | 3.50 | 11.03 | 1.76 |
| Pennsylvania | 1 | 6.27 | 3.05 | 2.06 | 72.89 | 3.83 | 11.90 | 1.90 |
| Ohio | 4 | 6.68 | 3.25 | 2.64 | 72.95 | 4.19 | 10.28 | 1.64 |
| Michigan | 5 | 6.27 | 2.79 | 2.72 | 72.34 | 3.42 | 12.46 | 1.99 |
| Indiana | 2 | 5.95 | 3.23 | 3.13 | 73.28 | 3.99 | 10.42 | 1.67 |
| Illinois | 4 | 6.37 | 3.08 | 2.67 | 71.84 | 3.66 | 12.38 | 1.98 |
| Wisconsin | 5 | 7.05 | 2.95 | 2.63 | 71.87 | 4.05 | 11.45 | 1.83 |
| Minnesota | 5 | 7.29 | 2.63 | 2.81 | 72.87 | 4.01 | 10.39 | 1.66 |
| Iowa | 4 | 6.27 | 3.08 | 2.71 | 71.37 | 4.01 | 12.56 | 2.01 |
| Nebraska | 1 | 7.48 | 3.00 | 2.70 | 71.12 | 3.35 | 12.25 | 1.96 |
| Dakota | 5 | 5.81 | 2.99 | 2.77 | 71.75 | 3.66 | 13.02 | 2.08 |
| Montana | 3 | 6.37 | 2.62 | 2.56 | 75.17 | 3.48 | 9.80 | 1.57 |
| South Carolina | 1 | 6.85 | 2.65 | 2.45 | 73.62 | 4.10 | 10.33 | 1.65 |
| Kentucky | 1 | 6.00 | 2.90 | 2.37 | 75.73 | 4.25 | 8.75 | 1.40 |
| Utah | 1 | 7.70 | 3.40 | 2.53 | 72.99 | 2.88 | 10.50 | 1.68 |
| Arizona | 1 | 6.26 | 2.90 | 2.63 | 74.30 | 4.28 | 9.63 | 1.54 |
| Washington | 1 | 5.95 | 3.50 | 2.98 | 70.97 | 4.35 | 12.25 | 1.96 |
| Oregon | 2 | 6.23 | 2.92 | 2.38 | 74.23 | 3.01 | 10.33 | 1.65 |
| California | 3 | 5.80 | 3.30 | 2.74 | 74.86 | 4.25 | 9.05 | 1.45 |
| Wyoming | 1 | 6.70 | 2.20 | 2.52 | 74.03 | 3.00 | 11.55 | 1.85 |
| Colorado | 1 | 8.15 | 2.77 | 2.87 | 68.99 | 3.92 | 13.30 | 2.13 |

The examination of the Canadian barleys is given in detail, as they were especially selected as graded specimens of the crop of 1885.

*Canadian Barleys.*

| Grade. | Serial number. | District. | Composition. Water. | Ash. | Oil. | Carbhydrates. | Fibre. | Albuminoids. | Nitrogen. | Weight. Weight per 100 grains. | Weight per bushel | Consistency. Mealy. | Half mealy. | Quarter mealy. | Little mealy. | Glassy. |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | P. ct. | P. ct | P. ct | Per ct | Per ct | Per ct | P ct | Grms. | Lbs. | | | | | |
| First quality | 6041 | A[1] | 7.58 | 2.98 | 2.70 | 73.49 | 3.10 | 10.15 | 1.62 | 2.910 | 54 8 | 16 | 32 | 24 | 20 | 8 |
| " " | 6044 | B[1] | 8.35 | 2.73 | 2.69 | 73.23 | 3.55 | 9.45 | 1.51 | 3.069 | 56.1 | .. | 48 | 36 | 12 | 4 |
| " " | 6047 | C[1] | 6.95 | 2.68 | 2.64 | 74.28 | 3.65 | 9.80 | 1.57 | 3.200 | 55.9 | 40 | 28 | 20 | 12 | .. |
| " " | 6050 | D[1] | 8.35 | 2.88 | 2.67 | 73.13 | 3.69 | 9.28 | 1.48 | 3.445 | 52.7 | 12 | 36 | 36 | 16 | .. |
| Average | .... | ... | 7.81 | 2.82 | 2.67 | 73.53 | 3.50 | 9.67 | 1.54 | 3.158 | 54.9 | 17 | 36 | 29 | 15 | 3 |
| Second quality | 6042 | A[2] | 7.85 | 2.95 | 2.72 | 72.76 | 3.22 | 10.50 | 1.68 | 2.818 | 54.5 | 36 | 40 | 12 | 12 | .. |
| " " | 6045 | B[2] | 7.03 | 2.80 | 2.80 | 73.46 | 3.76 | 10.15 | 1.62 | 3.056 | 54.7 | 16 | 36 | 28 | 16 | 4 |
| " " | 6048 | C[2] | 10.68 | 1.62 | 2.8 | 72.58 | 3.49 | 9.45 | 1.51 | 2.934 | 53.5 | 12 | 36 | 32 | 20 | .. |
| " " | 6051 | D[2] | 8.43 | 3.18 | 2.63 | 72.55 | 3.41 | 9.80 | 1.57 | 3.257 | 53.5 | 24 | 40 | 32 | 4 | .. |
| Average | .... | ... | 8.35 | 2.64 | 2.73 | 72.84 | 3.47 | 9.97 | 1.59 | 3.021 | 54.1 | 22 | 38 | 26 | 13 | 1 |
| Third quality | 6043 | A[3] | 8.78 | 2.70 | 2.69 | 72.35 | 3.50 | 9.98 | 1.60 | 3.012 | 52.4 | 36 | 28 | 24 | 8 | 4 |
| " " | 6046 | B[3] | 6.25 | 2.83 | 2.72 | 73.87 | 3.68 | 10.15 | 1.62 | 3.094 | 54.8 | 16 | 44 | 32 | .. | 8 |
| " " | 6049 | C[3] | 8.13 | 3.05 | 2.67 | 72.82 | 3.35 | 9.98 | 1.60 | 2.941 | 52.4 | .. | 40 | 44 | 16 | .. |
| " " | 6052 | D[3] | 7.93 | 3.18 | 2.74 | 73.47 | 3.35 | 9.33 | 1.49 | 3.226 | 54.3 | 20 | 32 | 24 | 20 | 4 |
| Average | .... | ... | 7.89 | 2.94 | 2.71 | 73.13 | 3.47 | 9.86 | 1.58 | 3.068 | 53.5 | 18 | 36 | 31 | 11 | 4 |
| Average A locality | .... | ... | 8.07 | 2.88 | 2.70 | 72.87 | 3.27 | 10.21 | 1.63 | 2.943 | 53.9 | 30 | 33 | 20 | 13 | 4 |
| Average B locality | .... | ... | 7.3 | 2.79 | 2.74 | 73.52 | 3.66 | 9.92 | 1.58 | 3.073 | 55.2 | 11 | 43 | 32 | 9 | 5 |
| Average C locality | .... | ... | 8.39 | 2.45 | 2.70 | 73.23 | 3.49 | 9.74 | 1.56 | 3.027 | 53.9 | 17 | 35 | 32 | 16 | .. |
| Average D locality | .... | ... | 8.24 | 3.08 | 2 68 | 73.05 | 3.48 | 9.47 | 1.51 | 3.309 | 53.5 | 19 | 36 | 31 | 13 | 1 |
| Grand average | .... | ... | 8.02 | 2.80 | 2.70 | 73.17 | 3.48 | 9.83 | 1.57 | 3.088 | 54.1 | 19 | 37 | 29 | 13 | 2 |

The districts in which the grain was grown are represented by the letters A, B, C and D, and included: A, the counties north of the central part of Lake Erie; B, the counties north of the northwestern part of Lake Ontario; C, the counties north of the central portion of Lake Ontario; D, the counties north of the northeastern portion of Lake Ontario, bordering on the Bay of Quinte.

B, C and D are considered to produce the best barleys, and especially D, the crop of which was, however, unfortunately injured by rain. The brightest grain is found in B.

As this barley forms a great portion of our supply, and is looked upon as the best, it will be considered first, and that of the United States compared with it.

Maercker found that the finest grain contained not more than 8 per cent. of albuminoids, and consisted of at least 80 per cent. of mealy kernels. These two factors, together with the brightness of the grain, he considered to be the characteristics by which its quality should be judged.

Of the twelve typical specimens of the Canadian crop, none were below nine per cent. of albuminoids, the average being 9.83, and only 6 contained 60 per cent. of kernels which were mealy or half mealy in structure. They cannot be said, therefore, to be equal to what is considered extremely fine barley in Germany. They do, however, reach, and in most cases exceed, the average production of foreign countries, and may be considered as of extremely good quality for samples from actual trade lots, and better than those produced the world over. In weight per bushel they are about the same as or slightly heavier than the average found by Maercker—52 pounds—and in moisture, as with all our grain, much dryer than the product of damper climates.

The differences in the different grades are marked almost entirely by brightness and perfection of the kernel, there being a remarkably close agreement in all other respects. This shows how important a factor climate and care in harvesting and handling is in enhancing or depreciating the value of the grain. The latter factor—care—is almost entirely within the control of the farmer, while meteorological conditions, of course, are not, except so far as the all-important point of selection of locality is within his power. Of the different districts, that north of Lake Erie produces the specimens richest in nitrogen, which would therefore be graded lowest as far as this influences our judgment, thus agreeing with

current opinion. In mealiness these specimens are much ahead of all the others, and this ought to more than balance the slightly higher percentage of albuminoids; but the summer rains eventually, by coloring the grain, have the greatest influence in determining its quality, and make the barley of this district the least desirable. The remaining districts north of Ontario produce grain much alike, that from the B district averaging heavier in weight per bushel, and that from D being a little less nitrogenous. As a whole, these Canadian barleys certainly form a very good standard of reference.

In comparing the barleys of the United States with those of Canada, it appears at once that, as a whole, the former average about as mealy in consistency as the latter. Examined by distribution geographically, the Eastern grain is found to be much less mealy than the Western, that of the Northwest being the richest in mealy kernels. Again, however, we find that but two out of sixty-four samples contained 80 per cent. or over of mealy or half-mealy kernels. In weight per bushel there is no variation from Canadian and foreign grain, but in size the barleys of the United States, as a whole, are larger than those of Canada. Unfortunately, we have no data for those of foreign production. The Eastern grain is no larger than the Canadian, and the average is increased by the large size of that from the Northwest and the Pacific Slope, which, at the same time, has an increased weight per bushel. The high percentage of albuminoids stored up in the peculiar climate of the Northwest, while an advantage in the wheat grain, would be a serious objection in barley. In fact, it appears that the average amount of albuminoids in the barley of the United States is greater than that of Canada, and far ahead of anything which Maercker would consider desirable. California alone is 1 per cent. below the average for the rest of the country, there being less than one-half per cent. difference from 11.50 per cent. in the average for all but California, which has 10.50 per cent. This is higher than was found in the Canadian grain, so that it may safely be said that the latter is at present the best, in so far as this constituent is to be considered as a test of quality.

In brightness, the samples from those portions of the country having a dry climate at harvest-time, especially the Pacific Slope and the Northwest, were far superior. This is an important feature in considering the best areas for the production of good malting barley; and while California as yet furnishes but little for brewing

purposes, it is without doubt one of our best fields, as with a proper selection of seed and system of cultivation it will not be difficult to reduce the albuminoid constituents to a figure corresponding with the brightness of the grain.

Among the numerous analyses, the following extremes were found:

| | Highest per cent. | State. | Lowest per cent. | State. |
|---|---|---|---|---|
| Water, | 9.15 | Minnesota. | 4.53 | California. |
| Ash, | 4.43 | California. | 1.50 | Minnesota. |
| Oil, | 3.54 | Indiana. | 2.06 | Oregon. |
| Carbhydrates, | 76.79 | Montana. | 68.99 | Colorado. |
| Crude fibre, | 4.65 | Ohio. | 2.64 | Illinois. |
| Albuminoids, | 14.88 | Dakota. | 8.75 | Kentucky & Or. |
| Weight per 100 grains, grams, | 4.900 | California. | 2.630 | Pennsylvania. |
| Weight per bushel pounds, | 60.2 | Utah. | 50.4 | Pennsylvania. |
| Per cent. of mealy and half-mealy kernels, | 100.00 | Montana. | 16.0 | Vermont. |

Dakota sustains its reputation for high nitrogen and Oregon for low, but the variations in this constituent are not as wide as in wheat; barley, and also rye, appearing to be less affected in this respect, although Maercker's experiments show that barley responds in its percentage of albuminoids readily to nitrogenous manuring. His seed was, however, very poor in albuminoids—7.7 to 8.0 per cent.—and would naturally increase when the conditions were made favorable.

In Koenig's collection of analyses of this grain he gives as the average of 127 specimens from all parts of the world:

| | Per cent. |
|---|---|
| Water, | 13.77 |
| Ash, | 2.69 |
| Oil, | 2.16 |
| Carbhydrates, | 64.93 |
| Crude fibre, | 5.31 |
| Albuminoids, | 11.14 |
| Total, | 100.00 |

This is but little different from the average product of the United States, and would point to the fact that our barley is as good for malting purposes as most of the world's production. Canada, in fact, as shown by the specimens which have been examined from there, is well above foreign averages in starchiness.

Experience and care have taught Canadians, in connection with their favorable climate, the means of producing an excellent grain, superior to other parts of the country. It seems quite possible for the farmers in many portions of the United States, and especially California, the climatic conditions of which are such as to avoid damaging summer rains, with not too dry and hot a climate, to increase our supply of barley of good quality.

There is one condition which in the case of wheat was found to be of evident effect. Although almost all the specimens examined were spring-sown grain, twelve of winter barley were found to contain but 10.05 per cent. of albuminoid, as compared to 11.42 in the spring varieties. Whether this could be made of any importance in practice cannot, of course, be decided except by the possibilities of the culture of winter barleys, which as yet seem to be small.

The greater inferiority of our average product is probably due more to attempts to grow it in localities of unsuitable climatic nature, or lack of care in cultivation, than to any other reason.

In a few samples the outer covering of the grain was detached and weighed—a point of interest to the brewer and malter. The extreme amounts were 16.94 and 12.55 per cent., not nearly as large as in oats. Following are the determinations:

*Barley—Percentages of Grain and Hulls.*

| Number. | | Grain. Per cent. | Hull. Per cent. |
|---|---|---|---|
| 4015, | California, | 83.06 | 16.94 |
| 4081, | Indiana, | 83.78 | 16.22 |
| 4090, | Indiana, | 83.70 | 16.30 |
| 4097, | Iowa, | 84.25 | 15.75 |
| 4107, | Iowa, | 85.72 | 14.28 |
| 4156, | Michigan, | 84.01 | 15.99 |
| 4166, | Minnesota, | 84.47 | 15.53 |
| 4179, | Minnesota, | 86.28 | 13.72 |
| 4202, | Nevada, | 84.93 | 15.07 |
| 4205, | Nevada, | 87.45 | 12.55 |
| 4220, | New York, | 84.96 | 15.04 |
| | Average, | 84.78 | 15.22 |

For many other details reference must be made to the original bulletin, which can be had upon application.

WASHINGTON, D. C., 1886.

# A METHOD FOR THE SEPARATION AND ESTIMATION OF BORIC ACID.

*With an Account of a Convenient Form of Apparatus for Quantitative Distillations.*

By F. A. Gooch.

In all successful methods for the estimation of boric acid, its comparative isolation is a necessary preliminary. Fortunately, the removal of nearly everything which interferes seriously with the proper execution of methods is not particularly arduous; but, of ordinarily occurring substances, two, silica and alumina—both very commonly associated with boric acid—are especially annoying in this regard. In the separation of alumina the trouble lies in the tendency of the precipitated hydrate to carry and retain boric acid,[1] so that the two cannot be parted by means of ammonia or ammonia salts; with silica, the difficulty is in removing it completely. The volatility of boric acid stands, of course, absolutely in the way of treating with acid and evaporating to dryness, and every chemist knows the vainness of attempting to precipitate silica by means of ammonia, ammonia salts, or zinc oxide in ammonia. In Stromeyer's method[2] the presence of silica is peculiarly harmful, since in passing to the condition of potassium fluosilicate this substance nearly quadruples its weight, and to free the potassium fluoborate from contaminating fluosilicate requires, according to Fresenius,[3] at least six treatments by solution in boiling water, the addition of ammonia, and evaporation to dryness. Wöhler[4] recommends evaporating the hydrochloric acid solution to dryness in a flask fitted to a condenser, collecting the distillate, reuniting the latter with the residue, and filtering from silica; and the operation is successful so far as the complete removal of silica is concerned; but the alumina, if present, is still in condition to give annoyance, and the other bases are yet to be separated.

Advantage has long been taken of the volatility of free boric acid with hydrofluoric acid or with alcohol to secure its removal from fixed substances, but so far as I know no attempt has been made

[1] Wöhler, Ann. d. Chem. u. Pharm. **141**, 268.
[2] Ann. d. Chem. u. Pharm. **100**, 82.
[3] Quant. Chem. Anal. 424.
[4] Handbook of Mineral Analysis, under "Datholite."

heretofore to secure its complete volatilisation and estimation in the distillate. The experiments which I proceed to describe are the result of an effort to accomplish this end.

Aside from the difficulties in manipulation and in the construction of apparatus which the use of hydrofluoric acid would involve, this reagent is otherwise plainly inapplicable to the purpose in view, and of other agents with which boric acid is known to volatilise freely methyl alcohol seems to present the most desirable qualities. Methyl alcohol, ethyl alcohol, and water are effective in the order in which they are named. Thus, to volatilise 1 gram of boric acid —the equivalent, speaking roughly, of about 0.5 gram of boric anhydride—two treatments with 10 cc. of methyl alcohol and evaporation to dryness in each case were adequate; for the volatilisation of 0.2 gram of boric acid were required two treatments of 10 cc. each of ethyl alcohol, succeeding an evaporation with 50 cc. of the same alcohol; and the residue of five evaporations of water over 0.4 gram of boric acid, taking in each case 50 cc. of water, followed by ignition, weighed 0.08 gram or one-fifth of the original weight. In the presence of water, methyl alcohol is not equally effective; amyl alcohol and sulphuric acid restrain its action similarly, doubtless by dilution simply, and hydrochloric acid seems to possess no advantage over water alone in developing the volatility of boric acid. As an example, an experiment may serve in which a solution of 0.4 gram of boric acid in 50 cc. of water, after being heated three times successively with 25 cc. of methyl alcohol until the boiling-point rose in every case nearly to that of water, and then evaporated to dryness, left a large residue which disappeared with a single charge of 25 cc. of methyl alcohol applied by itself.

From the residue of the evaporation of borax with hydrochloric, nitric, or acetic acid, methyl alcohol, as would naturally be predicted, volatilises the boric acid freely, though the presence of foreign material acts to a certain degree protectively and tends to diminish the rapidity with which the alcohol would otherwise effect extraction and volatilisation. In case, however, that acetic acid is used to break up the borate, the tendency of sodic acetate to lose acid and become alkaline simply by exposure to evaporation in its aqueous solution makes it necessary to insure the acidity of the residue of evaporation by adding a drop or two of acetic acid before repeating the treatment with methyl alcohol.

On the whole, methyl alcohol shows itself to be an excellent agent by which to secure the volatilisation of boric acid.

To retain free boric acid, magnesium oxide naturally suggests itself. According to Marignac,[1] it is effective, and if, in the course of analysis, it may have been partly converted to the chloride, it is easily regenerated by the action of heat and moisture. Marignac, it will be remembered, makes use of magnesia mixture—the chlorides of ammonium and magnesium with free ammonia—to fix the boric acid, evaporating the solution to dryness, igniting, extracting with boiling water, filtering, and weighing the residue, while the filtrate is again treated as before to recover traces of the borate, which has yielded to the solvent action of the water. During the drying and ignition the magnesium chloride yields hydrochloric acid, and it would seem scarcely possible that the magnesium borate should fail to show some loss of boric acid when both hydrochloric acid and moisture exert their action. Further, the presence of ammonia during evaporation does not prevent the volatilisation of boric acid,[2] and Marignac regards the addition of it from time to time as of doubtful use. So it appears natural to look for some loss under such conditions, and Marignac fully recognises the fact that the apparent accuracy of his method is due to the balancing of errors, the inclusion of foreign matter by the magnesium borate and the deficiency of the magnesia when precipitated as ammonio-magnesium phosphate together compensating for the loss of boric acid by volatilisation. To bring the matter to the test, the following experiments were made. In them and in all succeeding experiments the boric acid was weighed in solution, the standard of this having been fixed by dissolving in a known weight of water a known weight of fused boric anhydride prepared in a state of purity by frequent recrystallisation. The magnesium oxide employed was made from the pure chloride by precipitating by ammonium carbonate and igniting, and was free from lime and alkalies, and, as far as could be determined, otherwise pure. The whole operation of each experiment was conducted in one vessel, so as to avoid transfers. In all cases a weighed platinum crucible of 100 cc. capacity received a weighed portion of magnesia, and after ignition and subsequent weighing the weighed solution of boric acid was introduced. In Experiments (1) to (4) the magnesia was thoroughly stirred in the solution of boric acid, the evapora-

[1] Zeit. für Anal. Chem. **1**, 406. [2] Rose, Pogg. Ann. **80**, 262.

tion carried at once to dryness, and the crucible and residue ignited and weighed; in Experiments (5) to (8) the magnesia was dissolved, after the addition of the boric acid, in hydrochloric acid sufficient in amount to prevent the precipitation of magnesium hydrate on the subsequent addition of ammonia, ammonia introduced in considerable excess in (7) and (8), in distinct excess in (5) and (6), the whole evaporated and ignited, the residue moistened and again ignited, and this last treatment repeated until the residue ceased to yield vapor of hydrochloric acid when heated.

| | $B_2O_3$ taken. | MgO taken. | $MgO + B_2O_3$ found. | $B_2O_3$ found. | Error. |
|---|---|---|---|---|---|
| | Gram. | Gram. | Gram. | Gram. | Gram. |
| (1) | 0.1734 | 0.5005 | 0.6607 | 0.1602 | 0.0132— |
| (2) | 0.1804 | 0.4973 | 0.6660 | 0.1687 | 0.0117— |
| (3) | 0.1793 | 0.4949 | 0.6640 | 0.1691 | 0.0102— |
| (4) | 0.1794 | 0.4941 | 0.6627 | 0.1686 | 0.0108— |
| (5) | 0.1807 | 0.4984 | 0.6542 | 0.1558 | 0.0249— |
| (6) | 0.1789 | 0 4974 | 0.6687 | 0.1560 | 0.0229— |
| (7) | 0.1806 | 0.4944 | 0.6684 | 0.1740 | 0.0066— |
| (8) | 0.1789 | 0.4959 | 0.6672 | 0.1713 | 0.0076— |

From these results it appears plain that under the conditions of the experiments neither magnesia alone nor the magnesia mixture is efficient in fixing boric acid; but in Experiments (7) and (8), in which ammonia was employed in large excess, the loss of boric acid is least, so that it would seem to be the case that though ammonia is not a perfect preventive of volatilisation, it does exert a restraining action on the boric acid. That the magnesia mixture should be incapable of retaining entirely the boric acid present is, as has been pointed out, not surprising; but that the loss should be so great is rather startling, and more than suggests that the errors of Marignac's process are seriously excessive. The failure of magnesium oxide to hold back boric acid under the conditions of the experiment must be due to a cause other than that which determines the loss during the evaporation and ignition of the magnesia mixture, and for this it is natural to turn to the insolubility of the oxide—a quality likely to oppose some difficulty in the way of establishing complete contact between the boric acid and the magnesia during a short exposure. Direct tests of this point showed distinctly that mixtures of boric acid in water and

magnesia, when submitted at once to distillation, yielded boric acid to the distillate; but that, if the mixtures were permitted to stand some hours before distilling, the oxide passed to the semi-gelatinous condition of the hydrate, and retained the boric acid so firmly that turmeric failed to show the presence of the latter in the distillate. It is plain, therefore, that with sufficient preliminary exposure magnesia might be relied upon to retain boric acid; but inasmuch as long and perhaps somewhat indefinite periods of waiting are objectionable in any analytical process, it was thought best to try the effect of substituting lime for magnesia. Experiments (9) to (12), conducted like the previous ones, excepting only the use of carefully prepared and ignited calcium oxide instead of magnesium oxide, were made with this end in view.

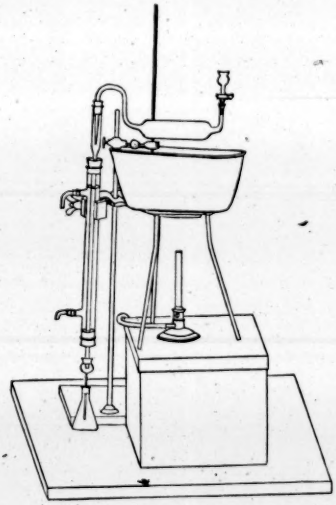
| | $B_2O_3$ taken. | CaO taken. | $CaO + B_2O_3$ found. | $B_2O$ found. | Error. |
|---|---|---|---|---|---|
| | Gram. | Gram. | Gram. | Gram. | Gram. |
| (9) | 0.1810 | 0.9737 | 1.1560 | 0.1823 | 0.0013+ |
| (10) | 0.1819 | 0.9750 | 1.1583 | 0.1833 | 0.0014+ |
| (11) | 0.1808 | 0.9922 | 1.1810 | 0.1818 | 0.0010+ |
| (12) | 0.1833 | 0.9715 | 1.1560 | 0.1845 | 0.0012+ |

These figures indicate sufficiently that there is no loss of boric acid by volatilisation when its aqueous solution is evaporated in contact with calcium hydrate; but, inasmuch as the comparative solubility of the latter is the quality which makes it effective where magnesia is not, it seemed desirable to test the action of calcium hydrate in alcoholic solutions, in which it is very insoluble. The experiment showed that when the solution of boric acid in methyl or ethyl alcohol is put upon lime and distilled at once, loss is apt to take place, and sometimes to a very considerable amount, but that a short period of digestion, with occasional stirring—from five to fifteen minutes—is sufficient to obviate danger of volatilisation of boric acid.

It appears, therefore, that, free boric acid being easily volatilised by means of methyl alcohol and fixed completely by calcic hydrate, the separation of the acid from almost everything with which it occurs ordinarily, and its estimation subsequently, depend only upon the practicability of distilling it from its compounds in such company that it may be retained by lime, and its amount determined by the increase in the weight of the latter. Unlike magnesium chloride, calcium chloride does not yield its chlorine readily under

the action of heat and moisture naturally retained; so that hydrochloric acid must not be present with boric acid, which is to be estimated in the manner described. Calcium nitrate and calcium acetate both yield the oxide without difficulty upon ignition, and nitric and acetic acids are suitable agents, therefore, for the liberation of boric acid previous to distillation.

The actual distillation presented at first some difficulty—for the repeated, thorough and rapid evaporation of a liquid charged with soluble or insoluble solid matter is apt to involve some mechanical transfer to the distillate of material which should remain in the residue—but the device of the following description solves the problem successfully.



The apparatus, which is shown in the accompanying cut, consists essentially of a retort, condenser, and bath for heating. For the last I have used a paraffine bath, as being on the whole the most convenient. The condenser is set vertically, to facilitate

changing the level of the retort within the bath, and to secure at the same time continual and thorough washing of the tube by its own condensations. The retort, somewhat like the well-known drying-tube of Liebig in general shape, is easily made of a pipette by bending the tube at one end to a right angle, at the other to a goose-neck, as shown. To the former end is fitted, by a rubber stopper or section of tubing, a glass funnel-tube provided with a stopcock; the end of the goose-neck passes tightly through a rubber stopper in the upper end of the condensing tube. This is essentially the apparatus, but it is convenient to attach to receive the distillate a small Erlenmeyer flask, which moves with the condenser and is joined to it, in the manner indicated in the figure, by means of a thistle-tube and a rubber stopper grooved to permit the free passage of air. In carrying out a distillation, the liquid to be distilled is introduced into the retort either by the funnel-tube or previous to its insertion, the glass cock is closed, the water started through the condenser, and the retort lowered into the hot paraffine, care being taken to begin the operation with the retort not more than half full and so inclined that only the rear dips below the surface of the bath. If the precaution to heat the retort at the start in this manner be overlooked, it may sometimes happen that the sudden and violent expulsion of air through the liquid will carry portions of it bodily into the goose-neck, and even into the condenser. With this point considered, the remainder of the operation presents no difficulty, and requires little care.

The size of the retort may be suited, of course, to the particular case in hand, but for most purposes a 200 cc. pipette makes a retort of convenient dimensions, neither too large for the distillation of small charges nor too small to permit the treatment of 100 cc. of liquid comfortably. The tube of the goose-neck should be wide enough to prevent the formation of bubbles in it; 0.7 cc. is a good measure for the interior diameter. It is of advantage to heat the bath to a point considerably above the temperature at which the liquid which is to be distilled boils—something between 130° C. and 140° C. does very well for water, and is not too high for methyl alcohol—and under such circumstances, and when the retort is entirely submerged, it often happens that evaporation takes place with extreme rapidity from the surface of the liquid in perfect quiet without actual boiling.

With such an apparatus the following experiments were made: The boric acid was weighed, as before, in solution, and, to bring the condition of the experiment to that of an actual analysis, 1 gram of pure sodium hydrate was added in solution, nitric acid or acetic acid to acidity and a little more, and the whole was introduced into the retort and distilled to dryness.

In those experiments in which nitric acid was employed, the methyl alcohol was introduced upon the residue thus dried in six successive portions of 10 cc. each, and distilled to dryness; but in order to break up the residue of sodium nitrate, which by its insolubility might effect to some extent the protection of the boric acid from the action of the alcohol, 2 cc. of water were introduced and evaporated between the second and third, and again between the fourth and fifth, distillations.

When acetic acid was made use of to free the boric acid, the six distillations with methyl alcohol were made as before; but sodium acetate being soluble in methyl alcohol, the intermediate treatments with water were unnecessary. With the fourth portion of methyl alcohol a few drops of acetic acid were added to preserve the acidity of the residue, which, as has been pointed out, tends to become alkaline under the treatment.

The residues of both processes of treatment were found to be free from boric acid by the exceedingly delicate test with turmeric, care being taken in the series of experiments in which nitric acid was used to oxidise nitrates by means of bromine (expelling the latter before making the test), and in the acetic acid series to acidify with hydrochloric acid sufficiently to counteract the tendency of the acetate by itself to brown the turmeric on evaporatien.

The lime to retain the boric acid in the distillate was ignited in the crucible in which the evaporation of the distillate was to be made subsequently, and then transferred to the receiving flask attached to the condenser, so that the boric acid might be fixed during the distillation. To prevent the caking of the lime by the action of the alcohol, it was slaked with a little water before the distillation was begun.

In Experiments (13) to (16) nitric acid was employed, and in (17) to (20) acetic acid was used, with the precaution noted, to liberate the boric acid.

| | $B_2O_3$ taken. | CaO taken. | $B_2O_3$+CaO found. | $B_2O_3$ found. | Error. |
|---|---|---|---|---|---|
| | Gram. | Gram. | Grams. | Gram. | Gram. |
| (13) | 0.1738 | 0.9647 | 1.1392 | 0.1745 | 0.0007+ |
| (14) | 0.1806 | 0.9639 | 1.1456 | 0.1817 | 0.0011+ |
| (15) | 0.1779 | 0.9665 | 1.1450 | 0.1785 | 0.0006+ |
| (16) | 0.1824 | 0.9739 | 1.1587 | 0.1848 | 0.0024+ |
| (17) | 0.1806 | 1.4559 | 1.6371 | 0.1812 | 0.0006+ |
| (18) | 0.1812 | 0.9720 | 1.1543 | 0.1823 | 0.0011+ |
| (19) | 0.1788 | 0.9986 | 1.1781 | 0.1795 | 0.0007+ |
| (20) | 0.1813 | 0.9527 | 1.1358 | 0.1831 | 0.0018+ |

In Experiments (13) to (16) the mean error amounts to 0.0012+ gram; in Experiments (17) to (20) the mean error is a little more than 0.0010+ gram. Throughout the entire series of experiments the tendency to yield figures slightly larger than the truth is manifest, but the error is quite within legitimate limits. The greatest care was taken to secure similarity of conditions under which the crucible and lime were weighed before and after the evaporation and absorption of boric acid, and the weight after ignition was taken in every case after cooling over sulphuric acid during a definite period of ten minutes, in order to eliminate as far as possible the effect of atmospheric condensation upon the large surface of platinum. Ignitions were always finished over the blast-lamp, and constancy of weights secured.

The results of both modes of treatment are on the whole satisfactory, and equally so.

In the presence of chlorides, it is of course impossible to employ nitric acid to free the boric acid. Oxalic, citric, and tartaric acids also liberate hydrochloric acid to a considerable extent from alkaline chlorides. It was found, however, that when acetic acid was distilled over sodium and potassium chlorides, only traces of hydrochloric acid passed into the distillate, and Experiments (21) to (23) were made to determine whether these amounts are sufficient to vitiate the separation of boric acid from alkaline chlorides by distillation in presence of free acetic acid. The details of treatment were identical with those of Experiments (17) to (20), excepting only the addition of 0.5 gram of sodium chloride to each portion before distillation.

| | $B_2O_3$ taken. | CaO taken. | $B_2O_3$+CaO found. | $B_2O_3$ found. | Error. |
|---|---|---|---|---|---|
| | Gram. | Gram. | Gram. | Gram. | Gram. |
| (21) | 0.1834 | 0.9842 | 1.1675 | 0.1833 | 0.0001— |
| (22) | 0.1831 | 0.9755 | 1.1593 | 0.1838 | 0.0007+ |
| (23) | 0.1761 | 0.9740 | 1.1523 | 0.1783 | 0.0022+ |

The mean error of these results is about 0.0009+ gram, and it is plain that the presence of sodium chloride does not materially change the conditions of the experiment. There seems, therefore, to be no reason why boric acid may not be separated by distillation from alkaline chlorides in presence of free acetic acid; but it was found that the presence of any considerable amount of potassium acetate is disadvantageous. Sodium acetate to a reasonable amount does not interfere with the favorable progress of the separation; but potassium acetate appears to require a much higher temperature for the expulsion of its water, and longer distillation.

When, therefore, chlorides are present in the salts from which boric acid is to be removed by distillation, the choice is open between two methods: the distillation may be made directly with an excess of acetic acid; or the hydrochloric acid may be first removed by means of silver nitrate, and the distillation of the filtrate proceeded with at once, or after precipitation of the excess of silver salt by means of sodium hydrate or carbonate, care being taken to acidify again sufficiently with nitric acid after the removal of the silver. Of these two modes of proceeding, I incline to the treatment with nitric acid and the removal of the chlorine by precipitation; and this method has been used with success by others as well as myself, for some months, in the analysis of waters carrying boric acid, and natural borates.

The process in either modification is fairly accurate and easily executed, and admits of very wide application. Insoluble compounds in which the boric acid is to be determined may be dissolved in nitric acid at once, or, if necessary, first fused with sodium carbonate; and, fortunately, nearly everything which is volatile in the subsequent treatment, and capable of forming with lime compounds not easily decomposable by heat, may be removed by known processes. The combination of fluorine, silica, and boric acid is perhaps most difficult to treat; but the precipitation and removal of the first as calcium fluoride from the aqueous solution of a fusion in alkaline carbonate may, it is believed, be effected with care, and the mode of procedure from that point is simple.

The number of distillations necessary depends, of course, upon the amount of boric acid treated. To remove 0.2 gram of boric anhydride completely to the distillate, six charges of methyl alcohol, of 10 cc. each, proved, as we have seen, to be ample.

The apparatus by the aid of which the distillation processes

which have been described were carried out has found useful application in a number of other processes. In the determination of free and albuminoid ammonia in waters which can be boiled quietly with difficulty, in the methods of estimating hydrofluoric acid which involve the expulsion of silicon fluoride from a mixture of the fluoride with sulphuric acid and silica, in the separation of iodine from bromides and chlorides by distilling with ferric sulphate and sulphuric acid, and of bromine from chlorides by means of permanganic acid, it has proved of value, and will doubtless be found convenient in many analytical processes in which quantitative separations by the distillation of liquids liable to spatter or boil explosively are involved.

## A METHOD FOR THE SEPARATION OF SODIUM AND POTASSIUM FROM LITHIUM BY THE ACTION OF AMYL ALCOHOL ON THE CHLORIDES.

*With Some Reference to a Similar Separation of the Same from Magnesium and Calcium.*

By F. A. Gooch.

For the quantitative separation of lithium from sodium and potassium, Mayer's method,[1] which is based upon the precipitation of lithium as the tribasic phosphate, and Rammelsberg's[2] mode of parting the chlorides by means of a mixture of anhydrous alcohol and ether in equal parts, have been available.

The method of Mayer grew out of the older process of Berzelius,[3] which consisted essentially in treating the solution of the alkaline salts with phosphoric acid and sodium carbonate in excess, evaporating to dryness, and extracting with cold water. The result of a single analysis of the product thus obtained was the testimony upon which Berzelius rested the belief and statement that the salt was a double phosphate of lithium and sodium, which left upon ignition sodium and lithium pyrophosphates in equal molecules; and on this Berzelius based his process for the estimation of lithium. Rammelsberg,[4] however, showed later that it was

[1] Ann. d. Chem. u. Pharm. **98**, 193.
[2] Pogg. Ann. **66**, 79.
[3] *Ibid.* **4**, 245.
[4] *Loc. cit.*

a tribasic phosphate which was actually obtained, and from his experiments arrived at the conclusion that the proportions of soda and lithia were variable within wide limits, the amounts of the former varying in the special cases investigated from 7.84 per cent. to 28.38 per cent.; and the same thing in substance was reiterated subsequently[1] in an account of a repetition of the work suggested by the criticism of Mayer. Mayer,[2] however, was unable to prepare under any conditions the double phosphate of Rammelsberg, and obtained invariably, when the preparation had been washed with sufficient care, trilithium phosphate free from sodium; but the point was made that the phosphate is apt to be contaminated with lithium carbonate when sodium carbonate is employed to bring about alkalinity. Mayer therefore modifies the method of Berzelius by substituting sodium hydrate for the carbonate; and, proceeding, evaporates to dryness, treats the dry mass with as much water as is needed to dissolve the soluble salts with the aid of heat, adds a drop or two of sodium hydrate if necessary to restore alkalinity, and then ammonia in volume equal to that of the water already added, sets aside at a gentle heat, filters only after twelve hours, and washes with a mixture of ammonia and water in equal parts. From the filtrate and first washings a small amount of the lithium phosphate is to be recovered by evaporation and the repetition of the former treatment. According to Mayer, the precipitation of the phosphate may be effected with equal completeness by boiling the solution, prepared as before, instead of evaporating it; but the objection to this mode of proceeding is the tendency of the liquid carrying the precipitate to bump explosively. Careful washing, somewhat prolonged, is essential to secure the complete removal of salts of sodium and potassium, and it is remarked that the purity of the precipitate is shown by its failure to cake when strongly ignited.

This is the mode of proceeding by which Mayer separates lithium from sodium and potassium, isolating it as presumably pure trilithium phosphate and weighing it as the anhydrous salt. In dealing with mixtures of the chlorides in which the proportion of the lithium salt is relatively small, the removal of the greater part of sodium and potassium chlorides by a preliminary treatment with absolute alcohol is recommended. The following table comprises the results of Mayer's test analyses of lithium carbonate in the first

[1] Pogg. Ann. **102**, 443. [2] *Loc. cit.*

seven, of lithium sulphate in the last two, recalculated with the use of the number 7—the figure now generally accepted as the atomic weight of lithium:

| $Li_3PO_4$ equivalent to salt taken. Grams. | $Li_3PO_4$ found. Grams. | Error. Grams. |
|---|---|---|
| 1.3586 | 1.3719 | 0.0133+ |
| 1.5172 | 1.5088 | 0.0084— |
| 0.7519 | 6.7580 | 0.0061+ |
| 0.9561 | 0.9510 | 0.0051— |
| 1.2651 | 1.2646 | 0.0005— |
| 1.2197 | 1.2230 | 0.0033+ |
| 0.8991 | 0.9018 | 0.0027+ |
| 1.1325 | 1.1236 | 0.0089— |
| 0.9715 | 0.9665 | 0.0050— |

Fresenius[1] found, on examining the method, that several repetitions of the treatment by evaporation and extraction were required to complete the recovery of all lithium phosphate, and advised that the operation be continued until residual lithium phosphate fails to appear. The results of Fresenius's experiments with lithium carbonate, recalculated with the use of the number 7 as the atomic weight of lithium, are given in the table appended:

| $Li_3PO_4$ equivalent to salt taken. Gram. | | $Li_3PO_4$ found. Dried at 100° C. Gram. | Ignited. Gram. | Error. Gram. |
|---|---|---|---|---|
| 0.7443 | after two treatments | 0.7243 | ... | 0.0200— |
| | " three " | 0.7385 | ... | 0.0058— |
| | " four " | 0.7433 | ... | 0.0010— |
| 0.9820 | | 0.9861 | ... | 0.0041+ |
| | | ... | 0.9826 | 0.0006+ |
| 1.6341 | | 1.6342 | ... | 0.0001+ |
| | | ... | 1.6305 | 0.0036— |

Thus it will be seen that in the nine experiments of Mayer the error ranges from 0.0133+ gram to 0.0089— gram, and that of the determinations of Fresenius from 0.0001+ gram to 0.0041+ gram for the dried precipitate, and from 0.0006+ gram to 0.0036— gram for the ignited precipitate.

If the tendency of lithium carbonate to fall in company with the phosphate were not to assert itself during the evaporations of solutions of salts of lithium in presence of sodium hydrate and in con-

[1] Zeit für anal. Chem. 1, 42.

tact with ordinary atmospheric air, it would surely be strange, and this point may be fairly set down as one of the weak ones of the method; but the gravest source of error, and that indicated most unmistakably throughout the whole history of the process—which has been recounted at some length for the purpose of emphasising this very matter—is the impossibility of preparing the lithium phosphate in anything like a condition of freedom from other alkaline phosphates without a careful and prolonged washing, which is sure to result in loss of the lithium salt by solution. When it is remembered that according to Mayer's determinations trilithium phosphate requires for solution only 2539 parts of water, or 3920 parts of a mixture of ammonia and water in equal portions, it is plain that the success of the method depends upon the ability of the analyst to wash to a condition of purity, and without loss of that which it is the purpose of the process to save, a precipitate peculiarly prone to retain foreign matter and soluble in the washing mixture in the proportion of ten milligrams to every 40 cc. of the latter. Of course washings will never be entirely saturated, nor will the precipitate be as soluble at the beginning of the operation as at the end, when the precipitant no longer exerts an action which tends to lessen solubility; but, in view of the difficulties which present themselves, it is sufficiently obvious that exact results obtained by Mayer's process owe their apparent accuracy to a fortuitous balance of errors. The difference of 0.0222 gram between the extremes of Mayer's experimental results should not be surprising; and, at the best, the process is tedious and not entirely trustworthy—facts of which its author was not unmindful.

In Rammelsberg's method of separating lithium chloride from the chlorides of sodium and potassium the sources of error are, in brief, the solubility of sodium chloride and potassium chloride in the ether-alcohol mixture, the influence which the presence of small amounts of water exerts upon the solubility of these same salts, the difficulty of bringing the chlorides to the anhydrous condition without decomposing the lithium chloride to a greater or less extent, and the mechanical difficulties of transferring the fused or crusted chlorides to a suitable receptacle for digestion and agitation in the solvent, and of extracting perfectly the soluble constituents of closely compacted matter. Of the last two items nothing need be said in explanation beyond simply noting them. The third is particularly important, inasmuch as the tendency of lithium chloride, first noted, I believe, by Mayer, to exchange

chlorine for oxygen when ignited in presence of water, results in the formation of lithium hydrate, or, in contact with products of combustion, lithium carbonate, both of which are insoluble in the mixture of ether and alcohol, and remain with the sodium and potassium chlorides. As to the effect of water in the mixture, an experiment of Mayer, in which it was found that 100 cc. of a mixture of alcohol of 96 per cent. and ether of 98 per cent. dissolved 0.1100 gram of sodium chloride, is instructive. In regard to the solubility of the chlorides of sodium and potassium in the mixture of anhydrous ether and alcohol, Rammelsberg's statement, that from 0.9770 gram of pure, strongly heated sodium chloride with an undetermined amount of lithium chloride the mixture extracted 0.0130 gram, is unfortunately meaningless in the absence of information concerning the amount of solvent employed. J. Lawrence Smith[1] found, in making an examination of this matter, that 10 cc. of the anhydrous ether-alcohol mixture extracted from 0.5 gram of sodium chloride 0.0005 gram, and from 0.5 gram of potassium chloride 0.0003 gram. Smith's mode of applying the method is better than the original; for, by taking care not to heat the mixed salts above 100° C., the danger of decomposing the lithium chloride is diminished, and by treating the dried salts with the ether-alcohol mixture in the capsule in which it is heated and weighed (protecting it by a small inverted bell-glass) the disadvantage of the transfer is avoided, but the danger is incurred that the mixed salts may not be thoroughly dried by heat so gentle. With this modification Smith obtained results which are rearranged in the following statement, and which do not throw a very favorable light upon the method:[2]

| NaCl taken. Gram. | KCl taken. Gram. | LiCl taken. Gram. | Weight dissolved. Gram. | Error. Gram. |
|---|---|---|---|---|
| 0.2000 | 0.2000 | 0.0080 | 0.0101 | 0.0021+ |
| 0.2000 | 0.2000 | 0.0884 | 0.0862 | 0.0022— |
| 0.2000 | 0.2000 | 0.8195 | 0.8341 | 0.0146+ |

[1] Am. Jour. Sci. [2] **16**, 56.

[2] Dr. Smith's language in the description of these experiments is somewhat ambiguous, but it is believed that these figures represent the meaning intended. After the presentation of the data of the first experiment given here with the correction of an obvious typographical error, it is said of the second and third experiments that "a similar mixture containing 18.20 per cent. of chloride of lithium furnished a residue of 17.65 per cent.," and "a similar mixture containing 67.20 per cent. of chloride of lithium gave a residue of 68.40." I have taken this to mean that in all three experiments 0.2 gram of sodium chloride and 0.2 gram of potassium chloride were employed with the different proportions of lithium chloride indicated for each experiment. At all events, if this is not the meaning of the language made use of, it is difficult to see a definite value in the experiments.

It is obvious, therefore, that neither the method of Rammelsberg nor that of Mayer may justly claim to be what a good process should be—accurate and rapid—and in the dilemma many chemists have been inclined to accept, with Bunsen,[1] the inherent disadvantage of an indirect process, and in a mixture of sodium and lithium chlorides calculate the percentage of each from the known weight of the mixture and its contents in chlorine, and in a mixture of the three chlorides calculate the percentage of each from the known weight of the mixture and the determined contents in chlorine and potassium. Here again, however, as in Rammelsberg's process, the difficulty of bringing the chlorides to a definite condition for weighing without decomposing the lithium chloride is an obstacle; and in case potassium is to be separated from large amounts of lithium by precipitation as potassio-platinic chloride, the concurrent precipitation of a similar salt of lithium, to which Jenzsch[2] has directed attention, may be the occasion of inexactness. So, the intrinsic unsatisfactoriness of indirect methods quite aside, it appears that in following Bunsen we have by no means all that is to be desired in an analytical method.

In looking about for better means for the separation of lithium from sodium and potassium, certain preliminary experiments on the behavior of the chlorides of these elements toward amyl alcohol gave very encouraging indications, and subsequent quantitative tests have borne out the hope that a successful method of separation might be based upon these relations.

In amyl alcohol the chlorides of sodium and potassium are highly insoluble, lithium chloride dissolves freely, and the attraction of amyl alcohol for water is so slight and its boiling-point so far above 100° C. that the latter may be expelled without difficulty by the aid of gentle heating.

When amyl alcohol is poured into a solution of lithium chloride in water, the liquid forms two layers, the aqueous solution of the salts at the bottom and the amyl alcohol now carrying a little water above. With the application of heat the water evaporates slowly, then boils, and, passing through the alcohol, escapes, until toward the end of the operation the residual lithium chloride collects in a viscous globule, and finally dissolves with the exception of a slight incrustation. If now the alcohol is cooled and a drop of strong hydrochloric acid added and brought in contact with the deposit,

[1] Ann. d. Chem. u. Pharm. **122**, 348. [2] Pogg. Ann. **104**, 102.

and the boiling repeated, the solution is complete. This deposit I take to be lithium hydrate, resulting from the decomposition of the chloride by the protracted action of water at a temperature near its boiling-point. The small amount of water which is added in and with the hydrochloric acid seems to exert no unfavorable influence, but rather to be beneficial in hastening the solution of the residue by securing immediate and sufficient contact.

In hot amyl alcohol lithium chloride appears to be a little more soluble than in the same reagent at ordinary temperatures, but the solubility under the latter condition only was determined. By boiling the solution until turbidity began to show, cooling, filtering, and then evaporating a known volume of the concentrated solution to dryness and weighing the residue after converting it to the sulphate, it was found that one part of lithium chloride was held dissolved in the cold in about fifteen parts of amyl alcohol, 10 cm.$^3$ of the solution containing in the mean 0.66 gram of the chloride.

When aqueous solutions of sodium chloride or potassium chloride are treated with amyl alcohol and boiled, the water disappears, as before, leaving first a globule of the concentrated solution and finally the crystalline salts. On continuing the boiling until a thermometer dipped in the liquid indicates the temperature at which the alcohol boils by itself, a slight additional precipitation, doubtless due to the expulsion of the water retained by the alcohol up to this point, takes place upon the walls of the containing vessel. The results of quantitative tests of the solubility of sodium and potassium chlorides are given in the following tables. The strength of the solutions of sodium chloride and potassium chloride was determined by evaporating weighed portions in a platinum crucible and drying at a temperature considerably below the melting point of the salt, and weighing. The solution of lithium chloride was standardised by treating a weighed portion with sulphuric acid in excess, evaporating, igniting at red heat, and weighing. The standards were fixed by Experiments (1) to (9).

| | Weight of Solution of NaCl taken. Grams. | Weight of NaCl found. Gram. | Weight of NaCl in 10 grams of Solution. Gram. | Mean. Gram. |
|---|---|---|---|---|
| (1) | 10.7110 | 0.1072 | 0.1001 | |
| (2) | 10.9419 | 0.1097 | 0.1003 | 0.1002 |
| (3) | 10.9325 | 0.1097 | 0.1003 | |

| | Weight of Solution of KCl taken. Grams. | Weight of KCl found. Gram. | Weight of KCl in 10 grams of Solution. Gram. | Mean. Gram. |
|---|---|---|---|---|
| (4) | 9.3045 | 0.1744 | 0.1874 | |
| (5) | 10.7225 | 0.2006 | 0.1871 | 0.1872 |
| (6) | 11.1974 | 0.2096 | 0.1872 | |

| | Weight of Solution of LiCl taken. Grams. | Weight of $Li_2SO_4$ found. Gram. | Weight of LiCl in 10 grams of Solution. Gram. | Mean. Gram. |
|---|---|---|---|---|
| (7) | 10.9280 | 0.1635 | 0.1156 | |
| (8) | 11.1480 | 0.1665 | 0.1153 | 0.1154 |
| (9) | 10.8790 | 0.1626 | 0.1154 | |

To determine the solubility of sodium chloride and potassium chloride in amyl alcohol, portions of the test solutions were weighed out, evaporated to a convenient bulk in platinum crucibles of 100 cc. capacity, amyl alcohol was added, the water expelled by boiling, and the heating continued for some minutes after the thermometer in the liquid indicated 132° C., the boiling-point of the alcohol employed. The liquid was then decanted with care and the residue dried at a temperature below its melting-point and weighed. When the chlorides are precipitated in the manner described, the deposit generally adheres so closely, and such particles as do remain loose settle so well, that the supernatant liquid may be decanted to the end without appreciable transportation of the insoluble residue. For the sake of perfect security, however, in this part of the manipulation the decanted liquid was filtered under gentle pressure upon asbestos, with the aid of the device which I have previously described for such purposes,[1] and, after gentle heating, the increase in weight of the felt and the containing perforated crucible added to the weight of the residual salt. In no case did this increase exceed a few tenths of a milligram, and often could not be detected.

As a source of heat, a bath in which the sand of the sand-bath is replaced by smooth asbestos board is a convenience, or a piece of asbestos board simply, about 30 cc. square, supported by a broad tripod and heated under the middle by a Bunsen burner, answers equally well to secure every gradation of heat without danger of igniting the evaporated alcohol.

As a control upon the results obtained by weighing the residue as described, the filtrate was evaporated in a large platinum crucible, and the residue thus left gently heated and weighed. Though

[1] This Journal **1**, 317.

the evaporation be conducted with extreme care, the residue is almost sure to show some blackening, due to the carbonisation of matter carried by the alcohol, which will not disappear entirely without the application of a degree of heat which the salts cannot bear without danger of volatilisation. The weight of the residue from the amyl alcohol itself is small — one portion of 50 cc. yielding 0.0003 gram and its mate 0.0007 gram—so that the data obtained by the evaporation of the filtered alcohol of the experiments, if not quite so trustworthy as the former testimony, may nevertheless serve the purpose of a very close control. Both sets of data are given in the following table:

| | Weight of NaCl taken. | Total Weight of NaCl found. | Weight found in Residue. | Weight found in Solution. | Volume of Residual Amyl Alcohol. |
|---|---|---|---|---|---|
| | Gram. | Gram. | Gram. | Gram. | Cc. |
| (10) | 0.1062 | 0.1067 | 0.1043 | 0.0024 | 52 |
| (11) | 0.1043 | 0.1047 | 0.1024 | 0.0023 | 46 |
| (12) | 0.1024 | 0.1030 | 0.1003 | 0.0027 | 51 |
| (13) | 0.1003 | 0.1008 | 0.0983 | 0.0025 | 45 |

Reducing these figures to a common level to show the action of the same amount of amyl alcohol in every case, we have:

| | Loss of NaCl to 100 cc. of Amyl Alcohol. | Mean. | Weight of NaCl found in Solution in 100 cc. of Amyl Alcohol. | Mean. |
|---|---|---|---|---|
| | Gram. | Gram. | Gram. | Gram. |
| (10) | 0.0037 | 0.0041 | 0.0046 | 0.0051 |
| (11) | 0.0041 | | 0.0050 | |
| (12) | 0.0041 | | 0.0053 | |
| (13) | 0.0044 | | 0.0055 | |

| | Weight of KCl taken. | Total Weight of KCl found. | Weight found in Residue. | Weight found in Solution. | Volume of Residual Amyl Alcohol. |
|---|---|---|---|---|---|
| | Gram. | Gram. | Gram. | Gram. | Cc. |
| (14) | 0.2091 | 0.2093 | 0.2074 | 0.0019 | 35 |
| (15) | 0.2074 | 0.2078 | 0.2059 | 0.0019 | 36 |
| (16) | 0.2059 | 0.2059 | 0.2040 | 0.0019 | 32 |
| (17) | 0.2040 | 0.2041 | 0.2015 | 0.0026 | 45 |

Derived from these figures we have:

| | Loss of KCl to 100 cc. of Amyl Alcohol. | Mean. | Weight of KCl found in Solution in 100 cc. of Amyl Alcohol. | Mean. |
|---|---|---|---|---|
| | Gram. | Gram. | Gram. | Gram. |
| (14) | 0.0049 | 0.0051 | 0.0054 | 0.0056 |
| (15) | 0.0041 | | 0.0053 | |
| (16) | 0.0059 | | 0.0059 | |
| (17) | 0.0056 | | 0.0058 | |

From these figures it appears that the total weight of chloride found is always a little greater than that taken, the mean increase being 0.0005 gram for sodium chloride, and 0.0002 gram for potassium chloride. It appears also that the residue left by the evaporation of the decanted and filtered amyl alcohol is greater than the loss put upon the chloride by the treatment—in the case of sodium chloride 0.0005 gram, in the mean, for every 50 cc. of amyl alcohol, which is about the quantity employed in the experiments; for potassic chloride 0.0002 gram, in the mean, for 40 cc. of amyl alcohol, which is approximately the quantity used in that case. It will be seen, therefore, that there exists for both salts an exact coincidence between the mean total excess found and the difference between the figures which indicate the solubility of the salts for the two methods of determination; and, taking this fact in conjunction with the results of the evaporation of amyl alcohol in blank—the mean residue being 0.0004 gram for 40 cc., and 0.0005 gram for 50 cc.—it seems to be brought out pretty clearly that the former set of figures represents more exactly the solubility of the salts, though the difference between the two series is not great. Resting, then, upon the former determinations, the solubility of sodium chloride may be taken as 0.0041 gram in every 100 cc. of anhydrous amyl alcohol, or one part in 30,000 parts by weight; and the solubility of potassium chloride, a little greater, is 0.0051 gram to 100 cc. of amyl alcohol, or one part in 24,000 by weight.

The conditions under which the salts are acted upon are such as should insure the complete saturation of the solvent, and in this connection it is interesting to note that for the quantities of material employed the discrepancy between comparable figures never exceeds 0.0005 gram.

In Experiments (10), (11) and (14), (15), the alcohol was decanted and filtered at once while hot; in (12), (13) and (16), (17), it was cooled to 30° C. before decanting; so it appears that the solubility of the salts is not influenced by changes of temperature within the range from 30° C. to 132° C.

Used simply to wash the precipitate, amyl alcohol cannot, of course, exert an effect at all comparable with that manifested in the experiments which have been described, but to know just what this action may be is important. Experiments (18) to (22) were undertaken, therefore, to elucidate this point.

Weighed amounts of the test solutions were evaporated nearly to saturation in small glass beakers, amyl alcohol added, and, as in the previous experiments, the whole heated until the salt had deposited and the residual alcohol had boiled quietly for some minutes at its ordinary boiling-point, the liquid decanted, filtered under gentle pressure by means of a weighed perforated crucible and felt of asbestos, the filtrate measured, the residue dislodged with the aid of a rubbing-rod, and transferred to the crucible and washed with anhydrous amyl alcohol, the washings being collected and measured. The crucible and contents were dried over a free flame turned low, so that the heat should not reach the melting point of the chlorides.

| | Weight of NaCl taken. | Weight of NaCl found. | Weight of NaCl found, corrected for Solubility in Residual Amyl Alcohol. | Error of Corrected Weight of NaCl found. | Volume of Residual Amyl Alcohol. | Volume of Amyl Alcohol in Washings. |
|---|---|---|---|---|---|---|
| | Gram. | Gram. | Gram. | Gram. | Cc. | Cc. |
| (18) | 0.0947 | 0.0937 | 0.0947 | 0.0000 | 24 | 44 |
| (19) | 0.1080 | 0.1074 | 0.1082 | 0.0002+ | 19 | 53 |
| | Weight of KCl taken. | Weight of KCl found. | Weight of KCl found, corrected for Solubility in Residual Amyl Alcohol. | Error of Corrected Weight of KCl found. | Volume of Residual Amyl Alcohol. | Volume of Amyl Alcohol in Washings. |
| | Gram. | Gram. | Gram. | Gram. | Cc. | Cc. |
| (20) | 0.1846 | 0.1837 | 0.1847 | 0.0001+ | 20 | 60 |
| (21) | 0.1964 | 0.1946 | 0.1961 | 0.0003— | 30 | 45 |
| (22) | 0.1857 | 0.1839 | 0.1854 | 0.0003— | 30 | 60 |

These results show very plainly that the solvent effect of anhydrous amyl alcohol used for washing under the conditions described is trifling in the extreme, and may be neglected utterly, providing the amount of the washing is not altogether disproportionate to the needs of the case.

We pass next to the consideration of the separation of the chlorides of sodium and potassium from lithium chloride. Weighed portions of the test solutions were concentrated and treated with amyl alcohol in the manner described until the precipitated salt was entirely free from water and the supernatant alcoholic solution of the lithium chloride boiled constantly at a point not far from that of the amyl alcohol employed. Then the liquid was cooled, a drop or two of strong hydrochloric acid added in accordance with the evident suggestion of the preliminary experiments previously mentioned, and heat again applied until the boiling had con-

tinued, as before, for some minutes at one point. The filtration, washing, drying, and weighing of the residue were effected as in Experiments (18) to (22). In those of the experiments in which the lithium salt in solution was also determined, the end was accomplished by evaporating the filtrate and washings to dryness, treating the residue with sulphuric acid, and igniting and weighing as lithium sulphate. In the following table the weight of insoluble chloride actually found is given in one column, and this weight, corrected according to the data previously determined for the solubility of the chloride in the residual amyl alcohol, appears in the column adjoining. So, also, the weight is given of the lithium sulphate actually found, and an adjacent column contains the result of correcting this weight for the accompanying sodium or potassium sulphate, or both, upon the hypothesis that these salts are neutral sulphates after the ignition. In the case of quantities so minute, the error which is introduced by such an assumption cannot be considerable, and in relation to this point Dittmar[1] maintains that comparatively large amounts of acid sodium or potassium sulphate may be reduced to the neutral salt by ignition simply. The figures of the column showing the weights of lithium chloride found are derived by calculation from the weights of lithium sulphate actually found. The other headings of the table are sufficiently intelligible without further explanation.

| | Weight of NaCl taken. | Weight of NaCl found. | Weight of NaCl found, corrected for Solubility in Amyl Alcohol. | Error in Weight of NaCl found. | Error in Corrected Weight of NaCl found. | Volume of Amyl Alcohol used. Residual. | Volume of Amyl Alcohol used. Total. |
|---|---|---|---|---|---|---|---|
| | Gram. | Gram. | Gram. | Gram. | Gram. | Cc. | Cc. |
| (23) | 0.1089 | 0.1092 | 0.1095 | 0.0003+ | 0.0006+ | 7 | 70 |
| (24) | 0.1084 | 0.1085 | 0.1090 | 0.0001+ | 0.0006+ | 12 | 80 |
| (25) | 0.1074 | 0.1067 | 0.1074 | 0.0007— | 0.0000 | 18 | 90 |

| | Weight of LiCl taken. | Weight of $Li_2SO_4$ found. | Weight of LiCl found. | Corrected Weight of LiCl found. | Error in Weight of LiCl found. | Error in Corrected Weight of LiCl found. |
|---|---|---|---|---|---|---|
| | Gram. | Gram. | Gram. | Gram. | Gram. | Gram. |
| (23) | 0.1298 | 0.1682 | 0.1299 | 0.1296 | 0.0001+ | 0.0002— |
| (24) | 0.1227 | 0.1592 | 0.1230 | 0.1225 | 0.0003+ | 0.0002— |
| (25) | 0.0116 | ... | ... | ... | ... | ... |

[1] Report on Researches into the Composition of Ocean Water, collected by H. M. S. Challenger during the Years 1873-1876, p. 18.

| | Weight of KCl taken. | Weight of KCl found. | Weight of KCl found, corrected for Solubility in Amyl Alcohol. | Error in Weight of KCl found. | Error in Corrected Weight of KCl found. | Volume of Amyl Alcohol used. Residual. | Volume of Amyl Alcohol used. Total. |
|---|---|---|---|---|---|---|---|
| | Gram. | Gram. | Gram. | Gram. | Gram. | Cc. | Cc. |
| (26) | 0.2051 | 0.2036 | 0.2053 | 0.0015— | 0.0002+ | 34 | 100 |
| (27) | 0.2022 | 0.2013 | 0.2032 | 0.0009— | 0.0010+ | 37 | 100 |
| (28) | 0.2109 | 0.2096 | 0.2104 | 0.0013— | 0.0005— | 16 | 100 |
| (29) | 0.0984 | 0.0970 | 0.0980 | 0.0014— | 0.0004— | 20 | 90 |

| | Weight of LiCl taken. | Weight of $Li_2SO_4$ found. | Weight of LiCl found. | Corrected Weight of LiCl found. | Error in Weight of LiCl found. | Error in Corrected Weight of LiCl found. |
|---|---|---|---|---|---|---|
| | Gram. | Gram. | Gram. | Gram. | Gram. | Gram. |
| (26) | 0.1256 | 0.1638 | 0.1265 | 0.1248 | 0.0009+ | 0.0008— |
| (27) | 0.1287 | 0.1677 | 0.1296 | 0.1277 | 0.0009+ | 0.0010— |
| (28) | 0.0113 | ... | ... | ... | ... | ... |
| (29) | 0.0113 | ... | ... | ... | ... | ... |

| | Weight of NaCl taken. | Weight of KCl taken. | Weight of NaCl + KCl found. | Corrected Weight of NaCl + KCl found. | Volume of Amyl Alcohol used. Residual. | Volume of Amyl Alcohol used. Total. |
|---|---|---|---|---|---|---|
| | Gram. | Gram. | Gram. | Gram. | Cc. | Cc. |
| (30) | 0.1053 | 0.1031 | 0.2064 | 0.2084 | 22 | 100 |
| (31) | 0.1051 | 0.0945 | 0.1988 | 0.2003 | 16 | 80 |

| | Weight of LiCl taken. | Error in Weight of NaCl + KCl found. | Error in Corrected Weight of NaCl + KCl found. |
|---|---|---|---|
| | Gram. | Gram. | Gram. |
| (30) | 0.0113 | 0.0020— | 0.0000 |
| (31) | 0.0113 | 0.0008— | 0.0007+ |

It will be noticed that in Experiments (23), (24), (26) and (27), the corrected error in the weight of the insoluble chloride has a positive value ranging from 0.0002+ gram to 0.0010+ gram with a mean of 0.0006+ gram; and that in Experiments (25), (28), (29), (30) and (31), the mean error is negative, amounting to less than 0.0001— gram, with a range from 0.0005— gram to 0.0007+ gram.

The point of difference between these two series of experiments is the amount of lithium chloride introduced, only a tenth of that used in the former being employed in the latter. It is plain that, when we are dealing with the larger amount, a larger portion tends to remain behind with the insoluble chloride; and here again we meet, though to a degree comparatively harmless, the inclination of lithium chloride to yield chlorine and pass to the form of lithium hydrate. When the lithium chloride is present in small amount, as in the latter group of experiments, there can be little left undis-

solved; and the spectroscope confirms the evidence of the figures of analysis as to the perfectness of the separation, by showing in such cases either no lithium at all or merely fugitive traces. If a single precipitation is sufficient to effect a satisfactory separation of the insoluble chlorides from small amounts of lithium chloride, it is natural to suppose that a repetition of the precipitation would be beneficial in treating larger quantities of lithium chloride. Experiments (32) to (37) illustrate the effect of a double precipitation. The chlorides were brought to filtration as before, the liquid was decanted as completely as possible, the precipitate washed slightly by decantation and redissolved in a little water, and the round of boiling, filtering, drying, and weighing carried to the end as before, care being taken to repeat the treatment with a drop of hydrochloric acid during the process of boiling. The two portions of residual amyl alcohol were measured apart, as well as the washings.

| | Weight of NaCl taken. | Weight of NaCl found. | Corrected Weight of NaCl found. | Error in Weight of NaCl found. | Error in Corrected Weight of NaCl found. | Volume of Amyl Alcohol used. Residual. | | Total. |
|---|---|---|---|---|---|---|---|---|
| | Gram. | Gram. | Gram. | Gram. | Gram. | I. Cc. | II. Cc. | Cc. |
| (32) | 0.1166 | 0.1163 | 0.1169 | 0.0003— | 0.0003+ | 8 | 8 | 150 |
| (33) | 0.1139 | 0.1127 | 0.1132 | 0.0012— | 0.0007— | 5 | 7 | 150 |

| | Weight of LiCl taken. | Weight of $Li_2SO_4$ found. | Weight of LiCl found. | Corrected Weight of LiCl found. | Error in Weight of LiCl found. | Error in Corrected Weight of LiCl found. |
|---|---|---|---|---|---|---|
| | Gram. | Gram. | Gram. | Gram. | Gram. | Gram. |
| (32) | 0.1287 | 0.1662 | 0.1284 | 0.1280 | 0.0003— | 0.0007— |
| (33) | 0.1347 | 0.1759 | 0.1359 | 0.1353 | 0.0012+ | 0.0006+ |

| | Weight of KCl taken. | Weight of KCl found. | Corrected Weight of KCl found. | Error in Weight of KCl found. | Error in Corrected Weight of KCl found. | Volume of Amyl Alcohol used. Residual. | | Total. |
|---|---|---|---|---|---|---|---|---|
| | Gram. | Gram. | Gram. | Gram. | Gram. | I. Cc. | II. Cc. | Cc. |
| (34) | 0.1155 | 0.1142 | 0.1152 | 0.0013— | 0.0003— | 10 | 10 | 100 |
| (35) | 0.1034 | 0.1017 | 0.1028 | 0.0017— | 0.0007— | 10 | 12 | 200 |
| (36) | 0.1914 | 0.1905 | 0.1912 | 0.0009— | 0.0002— | 3 | 11 | 90 |
| (37) | 0.1953 | 0.1939 | 0.1950 | 0.0014— | 0.0003— | 4 | 18 | 110 |

| | Weight of LiCl taken. | Weight of $Li_2SO_4$ found. | Weight of LiCl found. | Corrected Weight of LiCl found. | Error in Weight of LiCl found. | Error in Corrected Weight of LiCl found. |
|---|---|---|---|---|---|---|
| | Gram. | Gram. | Gram. | Gram. | Gram. | |
| (34) | 0.1125 | 0.1475 | 0.1139 | 0.1128 | 0.0014+ | 0.0003+ |
| (35) | 0.1251 | 0.1649 | 0.1274 | 0.1162 | 0.0023+ | 0.0011+ |
| (36) | 0.1263 | ... | ... | ... | ... | ... |
| (37) | 0.1282 | ... | ... | ... | ... | ... |

Thus it appears that, in the separation of the insoluble chlorides from the larger amounts of lithium chloride, the residue of two precipitations is substantially free from lithium.

For the sake of bringing the data in hand more directly into comparison, the corrected errors of the preceding determinations are tabulated again in the following statement:

| No. Exp. | Chloride. | Corrected error of insoluble chloride precipitated *once* from about 0.13 Gram of LiCl. | Corrected error of insoluble chloride precipitated *once* from about 0.013 Gram of LiCl. | Corrected error of insoluble chloride precipitated *twice* from about 0.13 Gram of LiCl. | Error in corrected Weight of LiCl. | Approximate Mean Error of LiCl. |
|---|---|---|---|---|---|---|
| | | Gram. | Gram. | Gram. | Gram. | Gram. |
| (23) | NaCl | 0.0006+ | ... | ... | 0.0002— | 0.0005— |
| (24) | " | 0.0006+ | ... | ... | 0.0002— | |
| (26) | KCl | 0.0002+ | ... | ... | 0.0008— | |
| (27) | " | 0.0010+ | ... | ... | 0.0010— | |
| (25) | NaCl | ... | 0.0000 | ... | ... | |
| (28) | KCl | ... | 0.0005— | ... | ... | |
| (29) | " | ... | 0.0004— | ... | ... | |
| (30) | NaCl+KCl | ... | 0.0000 | ... | ... | |
| (31) | " " | ... | 0.0007+ | ... | ... | |
| (32) | NaCl | ... | ... | 0.0003+ | 0.0007— | 0.0003+ |
| (33) | " | ... | ... | 0.0007— | 0.0006+ | |
| (34) | KCl | ... | ... | 0.0003— | 0.0003+ | |
| (35) | " " | ... | ... | 0.0007— | 0.0011+ | |
| (36) | " | ... | ... | 0.0002— | ... | |
| (37) | " | ... | ... | 0.0003— | ... | |
| Approx. mean, | | 0.0006+ | 0.00004— | 0.0003— | | |

Few processes in analytical chemistry are capable of yielding results more exact than these. The separation of from 0.1 gram to 0.2 gram of sodium or potassium chloride from a tenth of its own weight of lithium chloride is practically perfect in one operation, and from its own weight of lithium chloride the parting may be effected satisfactorily by two precipitations.

The points to be observed in executing the method may be recapitulated as follows:

To the concentrated solution of the chlorides, amyl alcohol is added and heat is applied, gently at first to avoid danger of bumping, until, the water disappearing from solution and the point of ebullition rising and becoming constant for some minutes at a tem-

perature which is approximately that at which the alcohol boils by itself, the chlorides of sodium and potassium are deposited and lithium chloride is dehydrated and taken into solution. At this stage in the operation the liquid is cooled and a drop or two of strong hydrochloric acid added to reconvert traces of lithium hydrate in the deposit, and the boiling continued until the alcohol is again free from water. If the amount of lithium chloride present is small it will now be found in solution, and the chlorides of sodium and potassium will be in the residue, excepting the traces, for which correction will be made subsequently. If, however, the weight of lithium chloride present exceeds ten or twenty milligrams, it is advisable at this point, though not absolutely essential to the attainment of fairly correct results, to decant the liquid from the residue, wash the latter a little with anhydrous amyl alcohol, dissolve in a few drops of water, and repeat the separation by boiling again in amyl alcohol. For washing, amyl alcohol previously dehydrated by boiling is to be used, and the filtrates are to be measured apart from the washings. In filtering it is best to make use of the perforated crucible and asbestos felt, and apply gentle pressure. The crucible and residue are ready for the balance after drying for a few minutes directly over a flame turned low. The weight of insoluble chlorides actually obtained in this manner is to be corrected by the addition of 0.00041 gram for every 10 cc. of amyl alcohol in the filtrate, exclusive of washings, if the insoluble salt is entirely sodium chloride, 0.00051 gram for every 10 cc. if potassium chloride constitutes the residue, and if both sodium and potassium chloride are present, 0.00092 gram; but, as in the experiments described, the entire correction may in any case be kept within narrow limits if due care be given to the reduction of the volume of residual alcohol before filtration. The filtrate and washings are evaporated to dryness, treated with sulphuric acid, the excess of the latter driven off, and the residue ignited to fusion and weighed. From the weight thus found the subtraction of 0.00050 gram is to be made if sodium chloride constitutes the precipitate, 0.00059 gram if potassium chloride alone is present in the residue, and 0.00109 gram if both of these chlorides are present, for every 10 cc. of filtrate exclusive of washings.

Amyl alcohol is not costly, the manipulations of the process are easy, and the only objectionable feature—the development of the

fumes of amyl alcohol—is one which is insignificant when good ventilation is available.

The process has been used for some months frequently and successfully, by others as well as myself, for the estimation of lithium in waters and minerals.

In this connection it seems best to include the record of certain experiments looking to the separation of the chlorides of sodium and potassium from the chlorides of magnesium and calcium. The behavior of magnesium chloride toward amyl alcohol is of interest, both with reference to the problem of separating sodium and potassium from lithium and magnesium when the latter are associated, and as concerns the parting of the alkalies from magnesium alone—a matter which is by no means perfectly simple—and Experiments (38) to (41) touch upon this topic.

The chlorides of sodium and potassium were weighed, as before, in solution; the magnesium chloride was obtained by dissolving in hydrochloric acid the oxide specially prepared and weighed as such. The process of treatment was identical with that just described for the separation of the chlorides of potassium and sodium from lithium chloride.

| | Weight of NaCl taken. | Weight of KCl taken. | Weight of NaCl+KCl found. | Corrected Weight of NaCl+KCl found. | Volume of Amyl Alcohol used. Residual, I. | Residual, II. | Total. |
|---|---|---|---|---|---|---|---|
| | Gram. | Gram. | Gram. | Gram. | Cc. | Cc. | Cc. |
| (38) | 0.1030 | 0.1064 | 0.2079 | 0.2100 | 23 | ... | 120 |
| (39) | 0.0967 | 0.1024 | 0.1976 | 0.2006 | 33 | ... | 100 |
| (40) | 0.1030 | 0.1073 | 0.2071 | 0.2093 | 13 | 11 | 100 |
| (41) | 0.1053 | 0.1093 | 0.2114 | 0.2142 | 12 | 18 | 100 |

| | Weight of MgO taken. | Error in Weight of NaCl+KCl found. | Error in Corrected Weight of NaCl+KCl found. |
|---|---|---|---|
| | Gram. | Gram. | Gram. |
| (38) | 0.1000 | 0.0015— | 0.0006+ |
| (39) | 0.1000 | 0.0015— | 0.0015+ |
| (40) | 0.1000 | 0.0032— | 0.0010— |
| (41) | 0.1000 | 0.0032— | 0.0004— |

The residues of Experiments (38) and (39), in which the separation was made by a single precipitation, carried traces of magnesia; those of (40) and (41), in which two precipitations were introduced, were found to contain in the one case no magnesia, and in the other an unweighable trace. These results point out a method by

which the chlorides of sodium and potassium may be obtained free from magnesia, while the small amounts of the former which pass into solution with the magnesium chloride are capable of accurate estimation; and there seems to be no reason why the separation of these alkaline chlorides from magnesium chloride and lithium chloride occurring together should not be effected in one operation, and the parting of the latter salts brought about by the familiar method of precipitating the magnesia in the cold as ammonium-magnesium phosphate.

Experiments (42) to (48), upon the separation of sodium and potassium from calcium by the action of amyl alcohol on the chlorides, yielded the figures of the following table. The mode of treatment was identical with that of the experiments with magnesia just described, excepting only the substitution of pure calcium oxide, specially prepared, for magnesium oxide.

| | Weight of NaCl taken. | Weight of KCl taken. | Weight of NaCl+KCl found. | Corrected Weight of NaCl+KCl found. | Volume of Amyl Alcohol used. Residual. I. | Residual. II. | Total. |
|---|---|---|---|---|---|---|---|
| | Gram. | Gram. | Gram. | Gram. | Cc. | Cc. | Cc. |
| (42) | 0.0859 | 0.1126 | 0.2177 | 0.2195 | 20 | ... | 100 |
| (43) | 0.1018 | 0.1057 | 0.2217 | 0.2235 | 20 | ... | 100 |
| (44) | 0.1096 | 0.0962 | 0.2112 | 0.2130 | 20 | ... | 100 |
| (45) | 0.0985 | 0.1018 | 0.2113 | 0.2130 | 19 | ... | 100 |
| (46) | 0.0914 | 0.1104 | 0.1968 | 0.2000 | 20 | 15 | 100 |
| (47) | 0.0997 | 0.1100 | 0.2080 | 0.2089 | 3 | 7 | 90 |

| | Weight of CaO taken. Gram. | Error in Weight of NaCl+KCl found. Gram. | Error in Corrected Weight of NaCl+KCl found. Gram. |
|---|---|---|---|
| (42) | 0.1000 | 0.0192+ | 0.0210+ |
| (43) | 0.1000 | 0.0142+ | 0.0160+ |
| (44) | 0.1000 | 0.0054+ | 0.0072+ |
| (45) | 0.1000 | 0.0110+ | 0.0127+ |
| (46) | 0.1000 | 0.0050— | 0.0018— |
| (47) | 0.1000 | 0.0017— | 0.0008— |

From these results it is plain that it is a far more difficult matter to dehydrate and dissolve calcium chloride than either magnesium chloride or lithium chloride. The separation of the chlorides of sodium and potassium from calcium chloride cannot be accomplished, for the quantities employed in these experiments, by a single precipitation; but the repetition of the treatment is effective.

In the residues of Experiments (46) and (47) calcium could not be found by the test with ammonium oxalate. In a case, therefore, in which the separation of sodium and potassium from lithium, magnesium, and calcium in one operation should be desirable, the end may probably be accomplished by means of the process here described.

Certain preliminary experiments with the nitrates of the bases under discussion indicate that these are susceptible of similar separation by the action of amyl alcohol; and the wide applicability in analytical operations of the general principle involved—the dehydrating of salts by means of amyl alcohol or other liquid of high boiling-point and appropriate solvent action—can scarcely be a matter of doubt.

## ON ORTHOTOLYLPHTHALIMIDE.

By M. Kuhara.

According to Von Gerichten,[1] it appears probable that phthalyl chloride is either $C_6H_4<\begin{matrix}CCl_2\\CO\end{matrix}>O$, or a mixture of this substance with the normal chloride. This led me to consider that phthalyl chloride might yield a substance isomeric with phthalimide by treating the former with ammonia. A few years ago, when in the laboratory of the Johns Hopkins University, working under the direction of Professor Remsen, I made a large number of experiments with the object of testing this idea. In the course of the experiments I obtained only once a substance quite distinct from phthalimide, although isomeric; but all efforts to get possession of this substance again entirely failed, and I was obliged to give up its further study. The details of the experimental results and some account of phthalyl chloride have already been published in this Journal **3**, page 26.

It has since occurred to me that if toluidine instead of ammonia is made to act upon phthalyl chloride, a substance isomeric with tolylphthalimide may probably be produced more readily, and I

[1] Ber. d. deutsch. chem. Gesell. **13**, 417.

therefore attempted the study of the action of orthotoluidine upon phthalyl chloride.

### *Action of Orthotoluidine upon Phthalyl Chloride. Orthotolylphthalimide.*

The phthalyl chloride and orthotoluidine used in the experiments were from Kahlbaum, of Berlin, and were purified by fractional distillation. Both substances had the right boiling-points. On mixing them together in the proportion of 1 mol. phthalyl chloride and 1 mol. orthotoluidine and gently warming, a violent reaction took place, with the evolution of hydrochloric acid, and the whole substance soon solidified. After washing the mass successively with water, hydrochloric acid and caustic soda, it was dissolved in alcohol and repeatedly crystallised. During crystallisation I paid a great deal of attention to each crop of crystals, as more than one kind of substance may possibly be formed at the same time. I could not, however, obtain more than one substance, so that phthalyl chloride seems not to be a mixture.

The substance thus obtained consists of groups of snow-white, microscopic short needles. It is insoluble in water, and difficultly soluble in cold alcohol and ether, more readily in hot glacial acetic acid and alcohol. It melts at 182°. The substance, dried at 100°, was analysed:

I. 0.2972 gram gave 0.8266 gram $CO_2$ and 0.1271 gram $H_2O$.
II. 0.30200 gram gave 0.8400 gram $CO_2$ and 0.1272 gram $H_2O$.
III. 0.2622 gram gave 0.7298 gram $CO_2$ and 0.1109 gram $H_2O$.

| | Calculated for $C_{15}H_{11}O_2N$. | | Found. I. | II. | III. |
|---|---|---|---|---|---|
| Carbon, | 180 | 75.95 | 75.85 | 75.86 | 75.91 |
| Hydrogen, | 11 | 4.64 | 4.75 | 4.68 | 4.69 |
| Nitrogen, | 14 | 5.91 | ... | ... | ... |
| Oxygen, | 32 | 13.50 | ... | ... | ... |
| | 237 | 100.00 | | | |

This substance is identical with "phthalorthotoluid," obtained by Froehlich[1] by fusing orthotoluidine and phthalic anhydride together, and its structure is represented by one of the two formulas below, depending upon the structure of phthalyl chloride:

I. $C_6H_4\langle\begin{matrix}CO\\CO\end{matrix}\rangle N.C_6H_4.CH_3$. II. $C_6H_4\langle\begin{matrix}C{=}N.C_6H_4.CH_3\\CO\end{matrix}\rangle O$

[1] Ber. d. deutsch. chem. Gesell. **17**, 2673. Inaugural dissertation, Berlin, März, 1885.

The formula I, however, seems to be more probable than II, inferring from the results of experiments which I will describe hereafter, and I therefore call the substance orthotolylphthalimide.

### *Orthotolylphthalamic Acid.*

On boiling orthotolylphthalimide with concentrated aqueous ammonia for a few hours, it gradually dissolved, and after driving off the excess of ammonia by further boiling, dilute hydrochloric acid then added precipitated an acid. The precipitate was dissolved in alcohol, in which it was very soluble, and repeatedly crystallised from the solution.

The acid crystallises in beautiful fine needles. It is soluble in water, more readily in alcohol. Its aqueous solution shows a feeble acid reaction towards litmus paper.

The air-dried acid was analysed and gave the following results:

| | Calculated for $C_{15}H_{13}NO_5$. | | Found. |
|---|---|---|---|
| Carbon, | 180 | 70.58 | 70.72 |
| Hydrogen, | 13 | 5.10 | 5.38 |
| Nitrogen, | 14 | 5.50 | ... |
| Oxygen, | 48 | 18.82 | ... |
| | 255 | 100.00 | |

This acid, which I call orthotolylphthalamic acid, is probably identical with "phthalorthotoluidinsäure," described by Froehlich.[1] The constitution of the acid, as far as can be judged from the analytical results, may be either

I. $C_6H_4<\begin{matrix}CO.NH.C_6H_4.CH_3\\CO.OH\end{matrix}$ or II. $C_6H_4<\begin{matrix}C<\begin{matrix}N.C_6H_4.CH_3.\\OH\end{matrix}\\COOH\end{matrix}$

### *Normal Lead Orthotolylphthalamate.*

This salt was prepared by precipitating with lead acetate from the neutral solution of ammonium orthotolylphthalamate obtained by boiling orthotolylphthalimide with concentrated ammonia, as in the case of the preparation of the free acid. The precipitate, well washed and dried at 100°, was analysed:

I. 0.66 gram gave 0.209 gram Pb.

II. 0.1168 gram gave 0.03716 gram Pb.

[1] Ber. d. deutsch. chem. Gesell. **17**, 2673. Inaugural dissertation, Berlin, März, 1885.

| | Calculated for $\left(C_6H_4<\begin{smallmatrix}CONH.C_6H_4.CH_3\\COO\end{smallmatrix}\right)_2Pb$. | Found. I. | II. |
|---|---|---|---|
| Lead, | 30.13 | 31.66 | 31.81 |

*Mono-Lead Orthololylphthalamate.*

This salt was prepared by precipitating with basic lead acetate from the neutral solution of ammonium orthotolylphthalamate. The precipitate, dried at 100°, was analysed:

I. 0.202 gram gave 0.0937 gram Pb.

II. 0.1342 gram gave 0.0622 gram Pb.

III. 0.2100 gram gave 0.0949 gram Pb.

| | Calculated for $C_6H_4<\begin{smallmatrix}CO-N-C_6H_4.CH_3\\COO\quad\quad>Pb\end{smallmatrix}$. | I. | Found. II. | III. |
|---|---|---|---|---|
| Lead, | 45.00 | 46.38 | 46.34 | 45.19 |

In I and II the amount of lead is a little higher than the theoretical, and this may be due to the formation of lead carbonate with basic lead acetate by the action of air during the precipitation and filtration of the salt. In III the amount of lead almost agrees with theory, and in this case the precipitation and filtration were conducted in an atmosphere of hydrogen in order to prevent the action of carbon dioxide upon the acetate.

Considering the formation of this mono-lead salt, one molecule of orthotolylphthalamic acid seems to contain two atoms of hydrogen replaceable by metal. On inspecting the two possible formulas of the acid represented above, the formula I contains two replaceable hydrogen atoms, of which one is that of carboxyl and the other is that of the imide group. It is well established that the imide hydrogen under some conditions has acid properties. Remsen and Stokes[1] give a list of salts of this kind, and those which were obtained by one of them are, for example:

Neutral lead anhydro-sulphaminephthalate, $C_6H_3<\begin{smallmatrix}SO_2>N\\CO\quad\quad>Pb.\\COO\end{smallmatrix}$

Neutral silver anhydro-sulphaminephthalate, $C_6H_3<\begin{smallmatrix}SO_2>NAg.\\CO\\COOAg\end{smallmatrix}$

Neutral potassium anhydro-sulphaminephthalate, $C_6H_3<\begin{smallmatrix}SO_2>NK.\\CO\\COOK\end{smallmatrix}$

[1] This Journal **6**, 269.

Several other examples of similar salts are found described in the Journals as:

Succimide gives $C_2H_4<\begin{matrix}CO\\CO\end{matrix}>NAg$ (Laurent, Gerhardt, Ann. d. Chemie **134,** 154).

$(C_2H_4<\begin{matrix}CO\\CO\end{matrix}>N)_2Hg$ (Dessaignes, Ann. d. Chemie **82,** 234).

Phthalimide gives $C_6H_4<\begin{matrix}CO\\CO\end{matrix}>NK$ (Cohn, Ann. d. Chemie **205,** 301).

$C_6H_4<\begin{matrix}CO\\CO\end{matrix}>NAg$ (Laurent, Jahresber. über die Fortschritte der Chemie, 1847–48, 590).

Dibenzamide gives $\begin{matrix}C_6H_5.CO\\C_6H_5.CO\end{matrix}>NAg$ (Ber. d. deutsch. chem. Gesell. **6,** 1392).

According to the formula II above, the acid possesses only one replaceable hydrogen, because it contains one alcoholic hydroxyl besides one carboxyl group. This hydroxyl group is, no doubt, tertiary alcoholic, and it is very improbable that the hydrogen of alcoholic hydroxyl can be replaced by a metal by treating with bases and metallic salts. It is very likely that orthotolylphthalamic acid and its mono-lead salt have the constitutions represented below:

$$C_6H_4<\begin{matrix}CO.NH.C_6H_4.CH_3,\\COOH\end{matrix} \qquad C_6H_4<\begin{matrix}CO.N-C_6H_4.CH_3.\\COO\end{matrix}>Pb$$

*Normal Silver Orthotolylphthalamate.*

On adding silver nitrate to the neutral solution of ammonium orthotolylphthalamate prepared by boiling orthotolylphthalimide with ammonia, there was at first produced a white, bulky precipitate of the salt, which soon lessened in bulk and changed to a crystalline form. The precipitate, dried at 100°, was analysed:

I. 0.1134 gram of the salt gave 0.03236 gram Ag.

II. 0.1404 gram of the salt gave 0.04190 gram Ag.

III. 0.1936 gram of the salt gave 0.05940 gram Ag.

| | Calculated as $C_6H_4<\begin{matrix}CO.NH.C_6H_4.CH_3.\\COOAg\end{matrix}$ | Found. I. | II. | III. |
|---|---|---|---|---|
| Silver, | 29.80 | 28.53 | 29.84 | 30.68 |

*Di-Silver Orthotolylphthalamate.*

When silver nitrate was added to the neutral solution of the ammonium salt, the white, bulky precipitate at first produced was

quickly filtered by means of a filter-pump before it changed into a crystalline state. The precipitate, dried at 100°, was analysed:

0.322 gram of the salt gave 0.152 gram Ag.

| | Calculated as $C_6H_4<\begin{matrix}CON<\begin{matrix}C_6H_4.CH_3\\Ag\end{matrix}\\COOAg\end{matrix}$ | Found. |
|---|---|---|
| Silver, | 46.04 | 45.84 |

*Mono-Barium Orthotolylphthalamate.*

This salt was prepared by boiling orthotolylphthalimide with pure baryta water. The excess of baryta was removed by means of carbonic acid, and the solution, filtered from barium carbonate, was concentrated. On adding a large excess of strong alcohol to this solution, the salt was precipitated. The precipitate, dried between 90° and 100°, was analysed:

0.1408 gram salt gave 0.084 gram $BaSO_4$ = .0493 Ba.

| | Calculated for $C_6H_4<\begin{matrix}CON-C_6H_4.CH_3\\COO>Ba\end{matrix}$ | Found. | Calculated for $(C_6H_4<\begin{matrix}CONH.C_6H_4.CH_3\\COO\end{matrix})_2Ba$, |
|---|---|---|---|
| Barium, | 35.12 | 35.01 | 21.24 |

*Methyl Derivatives of Orthotolylphthalamic Acid.*

The object of this experiment was to introduce a methyl group in place of the hydrogen in the imide group of the acid, expecting that if the formula I of the acid is correct, its methyl derivative, by decomposing with alkali, may produce monomethyl toluidine and phthalic acid. The experiment was conducted as follows: Finely pulverised orthotolylphthalamic acid was suspended in xylene, in which the acid partly dissolved, and then metallic sodium added in small pieces, and the whole heated in a flask over a calcium chloride bath for several days, during which the contents of the flask gradually changed into a shining, pasty mass, which was the sodium compound of the acid. An excess of methyl iodide was then added and the whole heated over a water bath. In a few hours the methyl compound was formed and sodium iodide settled to the bottom of the flask. Now, on adding a large quantity of water to the flask and shaking, some metallic sodium still left was converted into sodium hydrate and made the liquid strongly alkaline. The contents of the flask were then subjected to distillation with steam. The distillate, consisting mainly of xylene, was shaken up with dilute hydrochloric acid, and two

layers of liquids produced on standing were separated. By making the aqueous portion alkaline with sodium hydrate, an oil was precipitated, which was purified by distillation. The oil is colorless and smells like toluidine, and soon changes brown in air. It neither gives any characteristic reactions of toluidine nor gives an acetyl compound with either acetyl chloride or acetic anhydride, while toluidine and monomethyl toluidine readily yield acetyl compounds. Although I could not determine the exact boiling point of the substance, as the quantity was not quite enough for experiment, its properties seemed to be identical with those of the dimethyl-orthotoluidine of Thomsen[1] and Nölting.[2] It was then converted into the platinum double salt and several times crystallised from aqueous alcohol for purification. The double salt, dried at 100°, was analysed:

I. 0.1226 gram of the salt gave 0.0354 gram Pt.

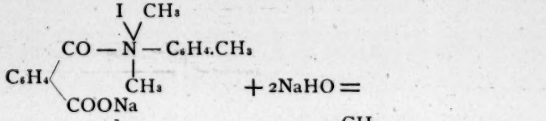
II. 0.1084 gram of the salt gave 0.0310 gram Pt.

| | Calculated as $2C_6H_4<^{CH_3}_{N(CH_3)_2}HCl + PtCl_4$. | Found. I. | II. |
|---|---|---|---|
| Platinum, | 28.99 | 28.87 | 28.59 |

The residual liquid in the flask was concentrated, and on adding hydrochloric acid to it a large quantity of phthalic acid was precipitated. In order to prove its identity it was converted into its potassium salt, which was dried at 100° and analysed:

| | Calculated as $C_6H_4(COOK)_2$. | Found. |
|---|---|---|
| Potassium, | 32.23 | 32.21 |

The formation of dimethyl-toluidine and phthalic acid may be explained thus: It is very probable that iodomethylate of orthotolylphthalamic acid would be formed, and that when the contents of the flask are distilled with steam the iodomethylate would be decomposed, as the liquid is strongly alkaline. The decomposition may be represented as follows:



$$C_6H_4(COONa)_2 + C_6H_4<^{CH_3}_{N(CH_3)_2} + NaI + H_2O.$$

[1] Ber. d. deutsch. chem. Gesell. **10**, 1586. [2] Ber. d. deutsch. chem. Gesell. **11**, 2279.

In order to confirm the formation of the iodomethylate, I repeated the experiment, which was conducted in the same way as before, by heating orthotolylphthalamic acid suspended in xylene with metallic sodium and methyl iodide. In this experiment xylene and all other soluble substances were extracted with ether, without adding any water to the flask. From the ethereal extract the ether was distilled off, and the residual liquid, consisting mainly of xylene, was distilled, together with water, by which all the xylene was separated. On evaporating the residual liquid to a syrupy consistency, the whole solidified to a semi-crystalline mass. It was found difficult to obtain the substance in a pure state, as it contained a large quantity of sodium iodide, and was little capable of crystallisation. On heating the semi-crystalline mass, it fused, giving a large quantity of methyl iodide, and again solidified. The substance may therefore be iodomethylate of orthotolylphthalamic acid. The substance left after giving off methyl iodide was also not easy to crystallise, so that it was difficult to purify. The substance, which was not pure, was analysed, so that it may throw light on its nature:

| | Calculated as $C_6H_4<\begin{matrix}CO.N<\begin{matrix}CH_3\\C_6H_4.CH_3\end{matrix}\\COONa\end{matrix}$. | Found. | Diff. |
|---|---|---|---|
| Sodium, | 9.41 | 7.9 | 1.51 |

In conclusion, I should say, the results of the above experiments can be best explained by assuming that phthalyl chloride has the commonly accepted formula. Further investigations are now in progress.

Chemical Laboratory, Medical Department,
University of Tokio, Japan, *August* 10, 1886.

## MANGANESE IN STEEL AND IRON.

By H. C. Babbitt.

In various communications which I have read upon those methods of determining manganese in iron and steel which depend upon the oxidation of the manganese to permanganic acid by the

action of lead peroxide in a nitric acid solution, all who do not absolutely condemn seem to agree that the presence of lead nitrate and the time of boiling have a great influence upon the accuracy of the results. A number of years ago I began to use a volumetric method of this description, and the difficulty of obtaining a reasonably pure lead peroxide, and the annoyance of preparing it for myself, led me to try red lead, $Pb_3O_4$, as an oxidising agent. After numerous experiments, by adding known quantities of manganese to an iron free from that element, and repeated checks by the acetate and other processes, with samples of steel varying from .05 to 2.00 per cent. of manganese, I became convinced of its utility, and for the past six years have used it on all grades of iron and steel, and occasionally upon spiegeleisen, with uniformly good results.

The discussion of this method has led me to make the following experiments, which may be of interest. The sample which I selected was a machinery steel of about .50 carbon, .04 silicon, and .09 phosphorus. The manganese by the acetate of soda and bromine process was obtained with the utmost care, using all possible precautions for accuracy.

By $NaC_2H_3O_2$ and Br = .515 per cent. manganese:

| | A. | B. |
|---|---|---|
| No. 1. | .516 | .512 per cent. of manganese. |
| 2. | .516 | .513 |
| 3. | .513 | .518 |
| 4. | .518 | .518 |
| 5. | .513 | .518 |
| 6. | .513 | .513 |

The method of procedure was as follows: .5 gram of steel was dissolved in about 15 cc. $HNO_3$ (1.15 to 1.20 sp. gr.), in a 50 cc. beaker. The solution was boiled till nitrous fumes ceased, red lead added—in A, one gram; in B, two grams. The solution was then diluted to about 30 cc. with hot water. In No. 1 the solution was simply stirred after its addition; in No. 2, heated to boiling; No. 3, boiled for one minute; No. 4, for two and a half minutes; No. 5, five minutes; No. 6, fifteen minutes. The solutions were then set aside to allow the residual lead peroxide to settle, the supernatant liquid decanted and the residue boiled with more hot water containing from 20 to 25 per cent. of nitric acid. These decantations are continued as long as they show a decided color of per-

manganic acid. When the manganese is below .60 per cent., one decantation and subsequent boiling is generally sufficient. The combined decantations are then filtered through asbestos and titrated with a standard reducing agent. If the presence of lead nitrate were fatal to accuracy, certainly the use of a compound which, when added to nitric acid, becomes a mixture of lead nitrate and lead peroxide, $2Pb(NO_3)_2 + PbO_2$, would be inadmissible; and the difference in time between the addition of hot water and boiling for fifteen minutes is an exceptionally wide limit. The only difference which I have ever found between filtering hot and cold is that occasionally lead peroxide will run through the filter and cause too high results from coincident oxidation of the reduced manganese. I have never been able to obtain uniformly accurate results with steel above .50 per cent. of manganese by taking an aliquot portion of the first decantation for titration, while companion analyses treated in the usual manner have yielded results which compared favorably with gravimetric methods.

CHESTER ROLLING MILLS, THURLOW, PA.

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**Contributions from the Agricultural Experiment Station of the University of Wisconsin.**

## METHODS OF BUTTER ANALYSIS.

BY F. W. A. WOLL.

The manufacture of artificial butter has during the last ten years attained vast dimensions both in America and Europe. With the increased manufacture and consumption, the methods of distinguishing between artificial and natural butter have become of greater importance, and the chemist is now frequently called upon to apply them. Of all the methods which have been proposed for chemical analysis of butter, those of Messrs. Reichert and Koettstorfer have found the most general application among American chemists, and they are also the only really practical methods which have thus far been devised. Hehner and Angell's method

is considered too lengthy and impracticable, while Baron Hübl's[1] method, though very good, is yet comparatively new and seems not to have become sufficiently known.

Of the 35,000,000 pounds of artificial butter said to have been manufactured in the United States in 1885, more than half, or nearly 20,000,000 pounds, is stated to have been made in Chicago. The greater part of this amount is called *butterine*, a mixture of oleo oil, neutral oil and natural butter. Butterine is commonly manufactured in two grades, called creamery and dairy butterine. The former contains 25 to 35 per cent., the latter 10 to 15 per cent. of natural butter.

As butterine is very frequently found in the market, samples of it are often sent to the chemist for analysis, and it then becomes desirable to determine the amount of natural butter it contains. This percentage may be calculated by means of the equations given by the authors of the methods mentioned above. To determine how accurately it is possible to determine the true amount of butter in a mixture by analysis according to Koettstorfer's and Reichert's methods, and otherwise to study the subject of butter analysis and artificial butter, the writer has been engaged in researches in this direction since January, 1886. To determine the first point, mixtures of natural butter fat and the crude product called *oleo oil* were made. These, which had both been previously analysed, were weighed out in fluid condition in the required proportions, mixed as well as possible, and then analysed according to the two methods. The following table gives the results:

TABLE I.

| Per Cent. Butter. | Koettstorfer. | | | Reichert. | | | Per Cent. of Butter Found by | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | Koettstorfer's Method. | | | | Reichert's Method. | | | |
| | Calculated. | Found. | Difference. | Calculated. | Found. | Difference. | Highest. | Lowest. | Average. | Difference. | Highest. | Lowest. | Average. | Difference. |
| | Mgr. | Mgr. | | Cc. | Cc. | | Per Ct. | Per Ct. | Per Ct. | | Per Ct. | Per Ct. | Per Ct. | |
| 20 | 200.8 | 201.4 | +0.6 | 2.98 | 3.11 | +0.13 | 36.3 | 1.7 | 18.3 | −1.7 | 21.2 | 19.8 | 20.5 | +0.5 |
| 40 | 206.2 | 207.3 | +1.1 | 5.81 | 6.39 | +0.58 | 55.0 | 20.4 | 37.6 | −2.4 | 45.9 | 43.0 | 44.5 | +4.5 |
| 50 | 208.5 | 209.0 | +0.5 | 6.55 | 7.08 | +0.53 | 60.4 | 25.8 | 42.9 | −7.1 | 51.1 | 47.9 | 49.5 | −0.5 |
| 60 | 211.5 | 212.7 | +1.2 | 8.65 | 9.06 | +0.41 | 72.1 | 37.6 | 54.7 | −5.3 | 67.6 | 61.8 | 63.9 | +3.9 |
| 80 | 217.7 | 215.6 | −2.1 | 10.37 | 11.56 | +1.19 | 81.3 | 46.7 | 63.9 | −16.1 | 85.1 | 79.5 | 82.2 | +2.2 |
| Average | | | 1.1 | | | 0.57 | | | | 6.5 | | | | 2.3 |

[1] Dingler, Polyt. Journal **253**, 281; also Fresenius' Analytische Zeitschrift **25**, 432.

The difference between the calculated and the observed number of mgrms. and cc. used in the analysis according to the two methods, must be ascribed to the difficulty of getting a perfectly homogeneous mixture. The numbers are averages of two or more determinations. The percentages of butter are calculated after the well-known equations,

$$x = (227 - n)\,3{,}17 \text{ and}$$
$$x = (7.30 \pm 0.24)\,(n - 0.3),$$

taking by Koettstorfer's method 232.4, 227 and 221.5 mgrms. as highest, average, and lowest value for genuine butter. The differences between the results calculated from the average numbers and the true percentages of butter are given in the table. In this case, where the butter had a very low value according to Koettstorfer's method (222.2 and 223.2 mgrms.), the difference was quite marked —on an average 6.5 per cent., with a highest value of 16.1 per cent. Reichert's method gives more closely accordant results, the average difference being 2.3 per cent. and highest 4.5 per cent. As will be seen, the method of Reichert gives the amount of genuine butter in a butterine with all desirable accuracy.

The results of analyses of thirty-seven samples of genuine butter, artificial butter and crude products are given below. As it may be of statistical interest, the results of the determinations of specific gravity and melting-point are also given; the former was determined by a 10 cc. specific gravity bottle at 37.7° C.,[1] and the latter by application of a glass bulb as devised by Hehner and Angell.[2] The weight of the glass bulb used was 3.386 grams.

The samples were obtained partly by direct application to the manufacturers, partly by purchase at grocery stores in Milwaukee, Wis., and Chicago, and partly by sampling on the spot in the manufactory of Armour & Co., Chicago.

TABLE II.

1.—*Genuine Butter.*

| No. | Sold as: Price. | Water. | Sp. Gr. | Melting-Point. | Koettstorfer. | Reichert. |
|---|---|---|---|---|---|---|
| 3 | Creamery Butter..... | 11.88 per cent. | .91274 | 34.5° C. | 225.0 mgr. | 13.05 cc. |
| 15 | Dairy Butter..... | .. | .91133 | 35.0 | 221.4 | 13.39 |
| 23 | " " ..... | .. | .91200 | 34.0 | 222.2 | 14.36 |

[1] Blyth, Foods, Composition and Analysis, London, 1882, p. 295.
[2] Hehner and Angell, Butter Analysis, p. 22.

2.—*Crude Products.*

| | | | | | | |
|---|---|---|---|---|---|---|
| 8 | Oleo Oil I ..... | 6.73 per cent. | .90356 | 29.2° C. | 192.0 mgr. | .04 cc. |
| 9 | " II (for export.)... | No. | .90354 | 25.7 | 191.7 | .19 |
| 24 | " ..... | No. | .90305 | 29.7 | 195.3 | .03 |
| 27 | " ..... | .. | .90368 | 27.7 | 195.0 | .12 |
| 37 | " ..... | .. | .90402 | 25.9 | 192.9 | .08 |
| 10 | Neutral Oil..... | 4.67 | .90552 | 37.8 | 190.8 | .03 |
| 25 | " " ..... | 7.49 | .90502 | 38.1 | 193.7 | No. |
| 28 | " " ..... | .. | .90536 | 38.3 | 195.5 | .15 |
| 36 | Sesame Oil..... | .. | .91326 | . | 185.1 | .17 |
| 22 | Cocoanut Oil..... | .. | .91743 | 24.5 | 257.9 | 3.64 |
| 11 | Crude Stearine ..... ..... | No. | .90124 (65° C.) | 55.3 | 193.6 | .37 |

3.—*Commercial Butters.*

| | | | | | | |
|---|---|---|---|---|---|---|
| 1 | Suspected Butter.. ..... | 8.77 per cent. | .91184 | 35.5° C. | 225.5 mgr. | 13.33 cc. |
| 26 | " " ..... | .. | .. | .. | 223 9 | 12.59 |
| 2 | " " ..... | .. | .. | .. | 230.5 | 14.69 |
| 26* | Butterine..... | .. | .90586 | 35.1 | 198.7 | 2.39 |
| 29* | Creamery Butter..... ..... | .. | .90576 | 34 5 | 201.2 | 2.93 |
| 12* | Creamery Butterine..... | 11.25 | .90554 | 34.5 | 202.2 | 4.43 |
| 13* | Dairy Butterine..... | 10.39 | .90449 | 33.9 | 194.4 | 1.59 |
| 14* | Oleomargarine..... | 9.89 | .90526 | 33.6 | 190.4 | .53 |
| 4 | Butter, Milwaukee, 24 c. | 9.42 | .91206 | 34.3 | 222 9 | 14.36 |
| 5* | " " 22 c. | 14.10 | .90604 | 34.6 | 193.1 | 1.54 |
| 6* | Butterine, " 20 c. | 11.19 | .90536 | 34.0 | 199.6 | 3.49 |
| 7* | " " 15 c. | 13.02 | .90440 | 32.0 | 194.2 | 2.16 |
| 17 | Best Cr'y, Chicago, 35 c. | .. | .91213 | 34.4 | 223.4 | 14.03 |
| 18 | Fancy Dairy, " 30 c. | .. | .91107 | 33.8 | 223.9 | 12.92 |
| 19* | " " " 22 c. | .. | .90502 | 33.2 | 195.4 | 1.57 |
| 20* | Dairy No. 1, " 16 c. | .. | .90574 | 32.5 | 197.3 | .02 |
| 21 | Best Cr'y, " 35 c. | .. | .91117 | 33.0 | 222.4 | 13.41 |
| 30* | Dairy, " 20 c. | .. | .91008 | 34.2 | 216.3 | 11.94 |
| 31* | Best Cr'y, " 30 c. | .. | .90504 | 36.1 | 197.1 | 1.29 |
| 32 | Best Dairy, " 25 c. | .. | .91166 | 36.5 | 232.0 | 14.02 |
| 33* | Elgin Cr'y, " 23 c. | .. | .90546 | 32.8 | 202.9 | 2.70 |
| 34 | Good Cr'y, " 25 c. | .. | .91120 | 32.0 | 222.3 | 13.78 |
| 35 | Good Dairy, " 20 c. | .. | .91166 | 32.3 | 226.2 | 14.28 |

NOTE.—* Artificial butter.

Genuine butter: Sp. gr. 0.914–0.91100, m.-point 32.0–36.5° C.; Koettstorfer: 221.4–232.4 mgr.; Reichert: 12.0–14.9 cc.

The samples No. 8–14 and 36 were from the manufactory of Armour & Co.; No. 24–26 from Fitts & Co.; No. 27–29 from Wm. J. Moxley; No. 37 from Fairbank Canning Co., all of Chicago. No. 3 was sent, on request, from Polar Creamery, Houston, Minn., firm Hostvet & Hourn. The suspected samples were sent to this station for analysis by private parties.

The three samples of genuine butter were pure beyond doubt. The samples are given the names under which they were sold. Out of eleven samples of butter bought at Chicago grocery stores at random, five were artificial butter. As will be seen, the determination of the melting-point is of no use in discriminating between a natural and an artificial butter. The specific gravity and Koettstorfer's or Reichert's methods, on the other hand, either singly or in combination, are decisive.

Oleo oil, neutral oil and sesame oil are used in the manufacture of artificial butter; oleo oil, made from the caul fat or the kidney

fat of beeves, has, on an average, specific gravity 0.90369; melting point, 27.6° C.; by Koettstorfer's method it requires 193.4 mgrms. KOH, and by Reichert's method .09 cc. deci-normal NaOH solution. Neutral oil, made from the leaf lard of hogs, has a specific gravity of 0.90530; melting-point, 38.1° C.; Koettstorfer's method requires 193.3 mgrm. KOH, and by Reichert's 0.16 cc. deci-normal NaOH solution. The specific gravity of genuine butter is usually considered to range from 0.91400 to .91200; seven of the eleven samples of genuine butter reported on above had a lower specific gravity than this limit. The lowest result was 0.91107.

The samples of artificial butter which were not oleomargarine—*i. e.* prepared only from oleo oil, neutral oil and a little cream or milk—contained butter in the following percentages, approximately:

| | | | |
|---|---|---|---|
| No. | 6, 20 per cent. | No. | 26, 15 per cent. |
| " | 7, 10 | " | 29, 20 |
| " | 12, 30 | " | 30, 80 |
| " | 13, 10 | " | 31, 10 |
| " | 19, 10 | " | 33, 20 |

The sample No. 30, containing 80 per cent. of natural butter, must have originated in some creamery, and would be more properly called adulterated butter; it would not pay for a manufacturer of artificial butter to use such a quantity of butter. As a rule, not more than 50 per cent. of pure butter enters the artificial product.

## ESTIMATIONS OF CARBONIC ACID IN THE AIR.

By Thomas C. Van Nüys and Benjamin F. Adams, Jr.

During the month of April, 1886, we made eighteen estimations of carbonic acid in the air, employing Van Nüys' apparatus, described in this Journal **8**, 190. These estimations were made in the University Park, one-half mile from the town of Bloomington. The park is hilly, thinly shaded, and higher than the surrounding country. The formation is sub-carboniferous and altitude 228 metres. There are no lowlands or swamps in the vicinity. The estimations were made at 10 A. M.

The air was obtained one-half metre from the ground and about 100 metres from any of the University buildings. The number of volumes of carbonic acid is calculated at zero C. and normal pressure 760 mm.

| Date. | Bar. Pressure. | Vols. $CO_2$ in 100,000 Vols. Air. | State of Weather. |
|---|---|---|---|
| April 2 | 743.5 | 28.86 | Cloudy, snow on ground. |
| " 5 | 743.5 | 28.97 | " " " " |
| " 6 | 735 | 28.61 | Snowing. |
| " 7 | 741.5 | 28.63 | Clear, snow on ground. |
| " 8 | 748 | 27.59 | " thawing. |
| " 9 | 747.5 | 28.10 | " " |
| " 12 | 744 | 28.04 | Cloudy. |
| " 13 | 744 | 28.10 | Clear. |
| " 14 | 743.5 | 28.98 | " |
| " 15 | 750.5 | 28.17 | Raining. |
| " 19 | 748 | 28.09 | Clear. |
| " 20 | 746 | 27.72 | " |
| " 21 | 746 | 28.16 | " |
| " 22 | 741.5 | 27.92 | " |
| " 23 | 740 | 28.12 | " |
| " 24 | 738.5 | 28.15 | " |
| " 25 | 738.5 | 27.46 | " |
| " 28 | 738 | 27.34 | " |

The average number of volumes of carbonic acid in 100,000 volumes of air is 28.16, the maximum number is 28.98, and the minimum 27.34. These results agree with estimations made within the last ten or fifteen years. Reiset[1] made a great number of estimations from September 9, 1872, to August 20, 1873, the average of which is 29.42. Six years later[2] he made many estimations from June to November the average of which is 29.78. The average of Schultze's[3] estimations is 29.2. The results of estimations of carbonic acid in the air, made under the supervision of Münz and Aubin[4] in October, November and December, 1882, at the stations where observations were made of the transit of Venus by astronomers sent out by the French Government, yield the average, for all stations north of the equator to latitude 29° 54′ in Florida, 28.2 volumes carbonic acid in 100,000 volumes air, and for all stations

[1] Comptes Rendus **88**, 1007.
[2] Comptes Rendus **90**, 1144.
[3] Chem. Centralblatt, 1872 and 1875.
[4] Comptes Rendus **96**, 1793.

south of the equator 27.1 volumes. The average of Claesson's[1] estimations is 27.9 volumes, his maximum number is 32.7, and his minimum is 23.7. It is apparent, from the results of estimations of carbonic acid of the air of various parts of the globe, by the employment of apparatus with which errors are avoided, that the quantity of carbonic acid is subject to slight variation, and not, as stated in nearly all text-books of science, from 4 to 6 volumes in 10,000 volumes of air; and it is further apparent that the law of Schloesing[2] holds good. By this law the carbonic acid of an atmosphere in contact with water containing calcium or magnesium carbonate in solution is dissolved according to the tension of the carbonic acid; that is, by an increased quantity its tension increases and more would pass in solution in the form of bicarbonates. On the other hand, by diminishing the quantity of carbonic acid in the atmosphere, some of the bicarbonates would decompose and carbonic acid pass into the atmosphere.

Schloesing's law has been verified by R. Engel.[3]

The results of estimations of bases and carbonic acid in the water of the English Channel lead Schloesing[4] to conclude that the carbonic acid combined with normal carbonates, forming bicarbonates, dissolved in the water of the globe is ten times greater in quantity than that of the atmosphere, and on account of this available carbonic acid, if the atmosphere should be deprived of some of its carbonic acid, the loss would soon be supplied.

As, in nearly all of the methods which were employed for estimating carbonic acid in the air, provision is not made for the exclusion of air not measured containing carbonic acid from the alkaline fluid before titrating or weighing, the results are generally too high and show a far greater variation than is found by more exact methods; for example, Gilm[5] found from 36 to 48 volumes; Levy's[6] average is 34 volumes; De Luna's,[7] 50 volumes; and Fodor's,[8] 38.9 volumes. Admitting that the quantity of carbonic acid in the air is subject to variation, yet the results of Reiset's and Schultze's estimations go to prove that the variation is within narrow limits.

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[1] Berichte der deutsch. chem. Gesellschaft **9**, 174. [2] Comptes Rendus **74**, 1552 and **75**, 70.
[3] Comptes Rendus **101**, 949. [4] Comptes Rendus **90**, 1410.
[5] Sitzungsber. d. Wien. Akad. d. Wissenschaften **34**, 257.
[6] Ann. d. l'Observ. d. Mountsouris, 1878 and 1879.
[7] Estudios químicos sobre el aire atmosférico, Madrid, 1860. [8] Hygien. Untersuch. **1**, 10.

# ON THE ACTION OF SULPHUROUS ANHYDRIDE ON BENZENE.

By Charles E. Colby and C. S. McLoughlin.

When benzene is treated with sulphuric anhydride, the elements of water are eliminated and a compound is formed containing the group $SO_2$ attached to two phenyl radicles. This body, first prepared by Mitscherlich,[1] was called by him sulpho-benzid; more recent investigators have given it the name of diphenyl-sulphone. It occurred to the authors that an analogous reaction might be possible between benzene and sulphurous anhydride, thus giving rise to a body containing the group SO combined with two phenyl radicles.

Benzene dissolves sulphurous anhydride in large quantity, but no reaction takes place between them unless condensing agents are present. Friedel and Crafts[2] found that a mixture of benzene and aluminium chloride absorbs sulphurous anhydride with great energy, forming benzene-sulphinic acid. They explain the reaction thus:

$$C_6H_6 + Al_2Cl_6 = C_6H_5Al_2Cl_5 + HCl,$$
$$C_6H_5.Al_2Cl_5 + SO_2 = C_6H_5SO_2Al_2Cl_5.$$

They then add water and thus obtain benzene-sulphinic acid:

$$C_6H_5SO_2Al_2Cl_5 + H_2O = C_6H_5.SO.OH + Al_2Cl_5OH.$$

We repeated these experiments, and, after several trials, proceeded in the following manner:

One hundred grams of benzene and 35 grams of aluminium chloride were placed in a flask fitted with a return condenser. The flask was heated on a water bath and a stream of sulphurous anhydride was passed through it by means of a tube dipping below the surface of the benzene. The sulphur dioxide was rapidly absorbed, the aluminium chloride gradually dissolved, and hydrochloric acid gas escaped. The operation was continued as long as the sulphurous anhydride appeared to be absorbed. The current of the anhydride was then stopped, but the flask was heated till no more hydrochloric acid gas was evolved. The contents of the flask were

[1] E. Mitscherlich, Liebig's Annalen der Chemie **12**, 308.
[2] Friedel and Crafts, Jahresbericht über die Fortschritte der Chemie, Giessen, 1878, 739.

allowed to cool and then poured into cold water. The precipitated aluminium hydrate was then dissolved and washed away by means of caustic soda. There remained a light yellow oil, which was separated from the aqueous liquid, dried with calcium chloride, and then allowed to evaporate at a gentle heat. The excess of benzene being thus removed, there was left a dirty yellow crystalline substance. This, when dissolved in xylene and left to itself, deposited small, transparent, isolated crystals, apparently belonging to the triclinic system. They were of a yellowish, waxy color, but on recrystallisation from petroleum ether they became perfectly white. Their melting-point lies between 70° and 71°; they are easily soluble in alcohol, ether, glacial acetic acid and benzene; difficultly soluble in cold petroleum ether, more readily in hot.

An ultimate analysis furnished the following results:

I. 0.2039 gram substance gave 0.5318 gram $CO_2$ and 0.0957 gram $H_2O$.

II. 0.2502 gram substance gave 0.6540 gram $CO_2$ and 0.1164 gram $H_2O$.

III. 0.1689 gram substance gave 0.1907 gram $BaSO_4$.

Collecting these figures:

| | I. | II. | III. | Theory for $(C_6H_5)_2SO$. |
|---|---|---|---|---|
| C | 71.13 | 71.28 | ... | 71.286 |
| H | 5.21 | 5.16 | ... | 4.950 |
| S | ... | ... | 15.51 | 15.843 |
| O | ... | ... | ... | 7.921 |
| | | | | 100.000 |

A portion of the substance was dissolved in ten times its weight of glacial acetic acid and oxidised by adding the calculated quantity of potassium permanganate. After diluting with water, and crystallising the resulting precipitate from alcohol, there were obtained white crystalline plates of diphenyl-sulphone melting at 128°. The yield was almost theoretical. Another portion of the substance on treatment with two molecules of metallic sodium furnished diphenyl-sulphide boiling at 272°. These results lead us to the conclusion that the body produced by the action of sulphurous anhydride on benzene in presence of aluminium chloride is diphenyl-sulphoxide, $C_6H_5 - SO - C_6H_5$.

We have also tried the action of thionyl chloride, $SOCl_2$, on

benzene in presence of aluminium chloride. The reaction is represented thus:

$$2C_6H_6 + SOCl_2 = (C_6H_5)_2SO + 2HCl,$$

and is analogous to that of oxy-chloride of carbon (phosgene) on benzene in presence of aluminium chloride.

In preparing diphenyl-sulphoxide by means of thionyl chloride we proceeded as follows:

Fifty grams of benzene and 16 grams of thionyl chloride were placed in a flask fitted with a return condenser, the flask being immersed in cold water. Aluminium chloride was then added, in small portions, to the mixture in the flask. The aluminium chloride was rapidly dissolved and hydrochloric acid gas escaped. The addition of aluminium chloride was continued at intervals as long as hydrochloric acid gas was given off. Altogether 30 grams of aluminium chloride were used. Toward the end of the operation 20 grams more of benzene were added to make the mixture more fluid. When fresh addition of aluminium chloride produced no further evolution of hydrochloric acid gas, the flask, with its return condenser still attached, was heated on a water bath for half an hour, then allowed to cool and the contents poured into cold water. A thick yellow oil resulted which floated. This oil was washed with water and then gently warmed in a dish to remove surplus benzene. On cooling there remained a yellowish, waxy mass, which when crystallised from petroleum ether furnished white crystals of the same form as those described above and possessing the same properties. Their melting-point was 70.5°. The ultimate analysis of these crystals showed the same composition as those obtained by the action of sulphurous anhydride on benzene:

I. 0.2500 gram substance gave 0.6523 gram $CO_2$ and 0.1117 gram $H_2O$.

II. 0.1000 gram substance gave 0.1160 gram $BaSO_4$.

| | I. | II. | Theory for $(C_6H_5)_2SO$. |
|---|---|---|---|
| C | 71.16 | ... | 71.286 |
| H | 4.96 | ... | 4.950 |
| S | ... | 15.93 | 15.843 |
| O | ... | ... | 7.921 |
| | | | 100.000 |

From 50 grams of benzene and 16 grams of thionyl chloride we

obtained 21 grams of the pure diphenyl-sulphoxide. The theoretical yield is a little more than 26 grams.

It is interesting to note that the diphenyl-sulphoxide fills a gap between the sulphide and sulphone, just as phenyl-sulphinic acid is intermediate between the sulphhydrate and the sulphonic acid:

$\left.\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right\}$ S Diphenyl-Sulphide. $\left.\begin{matrix}C_6H_5\\H\end{matrix}\right\}$ S Phenyl-Sulphhydrate.

$\left.\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right\}$ SO Diphenyl-Sulphoxide. $\left.\begin{matrix}C_6H_5\\HO\end{matrix}\right\}$ SO Phenyl-Sulphinic Acid.

$\left.\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right\}$ $SO_2$ Diphenyl-Sulphone. $\left.\begin{matrix}C_6H_5\\HO\end{matrix}\right\}$ $SO_2$ Phenyl-Sulphonic Acid.

*Nitration of the Diphenyl-Sulphoxide.*

This operation appears to be difficult, since the nitric acid exerts an oxidising influence on the diphenyl-sulphoxide. The calculated quantities of diphenyl-sulphoxide and of sodium nitrate were dissolved in separate portions of concentrated sulphuric acid. The two solutions were then mixed together and the mixture heated on a water bath for two hours. The mixture was then poured into cold water, and the resulting yellow precipitate, after washing, was dissolved in alcohol and allowed to crystallise. By repeated fractional crystallisation the result of the nitration was separated into three products. *First:* Light yellow crystals, consisting of small rhombic plates, only slightly soluble in alcohol, easily soluble in glacial acetic acid. They had a melting-point of 163°, and we think they are the dinitro-sulpho-benzid described by Gericke.[1] *Second:* Yellow, indistinct, microscopic crystals melting at 116° and readily soluble in cold alcohol, very soluble in ether, benzene, glacial acetic acid and carbon disulphide. Ultimate analysis furnished the following data, showing that it is the dinitro-compound of diphenyl-sulphoxide:

I. 0.2504 gram substance gave 0.4552 gram $CO_2$ and 0.0691 gram $H_2O$.

II. 0.2505 gram substance gave 0.4532 gram $CO_2$ and 0.0677 gram $H_2O$.

III. 0.0500 gram substance gave 0.0401 gram $BaSO_4$.

IV. 0.2000 gram substance gave 18 ccm. nitrogen measured at 30°, and 765.6 mm. corresponding to 0.01966 gram nitrogen.

[1] Gericke, Liebig's Annalen der Chemie, 100–211.

| | I. | II. | III. | IV. | Theory for Dinitro-Diphenyl-Sulphoxide. $(C_6H_4NO_2)_2SO$. |
|---|---|---|---|---|---|
| C | 49.57 | 49.34 | ... | ... | 49.31 |
| H | 3.06 | 3.00 | ... | ... | 2.75 |
| S | ... | ... | 11.01 | ... | 10.95 |
| N | ... | ... | ... | 9.83 | 9.59 |
| O | ... | ... | ... | ... | 27.40 |
| | | | | | 100.00 |

The third product of the nitration of diphenyl-sulphoxide seems to be an oil at ordinary temperatures. We have not yet determined its composition or its properties.

We reserve for a future article the results of our work on other substitution derivatives of the diphenyl-sulphoxide, and also on some of its condensation-products.

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# NOTES.

## *Germanium.*

This new element, which is exciting considerable attention among chemists, was discovered by Clemens Winkler, of Freiburg, in the early part of the year 1886. The constant error of about six per cent. in the result of his analysis of a comparatively simple mineral led him to suspect the presence of one or more new elements.

Such a suspicion was well founded, and, as the result of an exceedingly careful and painstaking investigation, he succeeded in isolating a new substance, which conducts itself in every way like an element; and, what is of still more general interest, a careful study of this new simple body and the compounds which it forms with other elements shows, it can be said almost conclusively, that it agrees in properties with the *eka-silicium* of Mendelejeff.

The silver ore from which germanium is obtained, and which is now known in mineralogy as argyrodite, is found in the neighborhood of Freiburg, and the analysis of the mineral has shown it to have the composition represented by the formula $3Ag_2S,GeS_2$. According to this, it may be regarded as a sulpho-salt for which mineralogy furnishes no analogues.

In order to extract germanium, the mineral in which it occurs is fused with an equal weight of a mixture of equal parts of flowers of sulphur and soda ash; the fused mass is then boiled with caustic soda, and the solution thus obtained is neutralised with dilute sulphuric acid; this is then filtered; to the filtrate dilute sulphuric acid is again added, when the sulphide of germanium is thrown down. This is filtered off and washed with dilute acid containing hydrogen sulphide; and finally, by treating the washed precipitate with strong nitric acid and evaporating to dryness, germanium oxide is obtained, which may be reduced either by heating to redness in a current of hydrogen, or by heating a mixture of the oxide and starch in a covered crucible. In this way germanium is obtained in the form of a dark gray powder, which melts under borax glass at 900° C.

The element is found to be extraordinarily brittle, and to have a strong tendency to crystallise in the regular system. It has a fine metallic lustre; in color it is grayish-white, considerably whiter than zirconium. At 20.4° C. it has been found to have a specific gravity of 5.469.

Germanium is not acted on by hydrochloric acid, but is easily dissolved in aqua regia. Nitric acid converts it into a white oxide with liberation of the oxides of nitrogen. Treated with concentrated sulphuric acid, it yields a white, crystalline sulphate, sulphur dioxide being liberated in a constant stream during the action. It is not acted on by potassium hydroxide in the cold.

The atomic weight of germanium has been determined by two entirely different methods: 1st, volumetrically, by determining the amount of chlorine in the tetra-chloride, $GeCl_4$, according to the method of Volhard; and, 2d, from calculations based on the wave lengths of certain lines in the spark-spectrum. By the former method the atomic weight has been found to be 72.32; by the latter 72.28. The very close agreement of this number 72.28, as representing the atomic weight of the new element, with that of the unknown element between gallium and arsenic on the one hand and titanium and zirconium on the other, in the table of Mendelejeff, has naturally led to a very careful comparison of the properties of germanium with those of eka-silicium, whose properties were predicted by Mendelejeff as early as 1871. The results of the comparison will be best seen by presenting them in tabular form:

| *Eka-Silicium, Es.* | *Germanium, Ge.* |
|---|---|
| Atomic weight, about 72. | Atomic weight, 72.32 and 72.28. |
| Density, 5.5. | Density, 5.469. |
| Atomic volume, 13. nearly. | Atomic volume, 13.25. |
| Will form an oxide, $GeO_2$. | Forms an oxide, $GeO_2$. |
| Sp. gr., 4.7. | Sp. gr., 4.703. |

| *Eka-Silicium, Es.* | *Germanium, Ge.* |
|---|---|
| Easily obtained by reduction with carbon or sodium. | Easily obtained by reduction with carbon or hydrogen. |
| A dirty gray metal, fusible with difficulty, forming the oxide when heated in air. | A gray-white metal, fusing at 900° C., and forming the oxide when heated in air. |
| Will form a chloride of the composition $EsCl_4$, which will boil near 100° C., probably lower. $EsO_2$ will form a hydrate soluble in acids. This solution will probably decompose readily, yielding an insoluble hydrate. | Forms a chloride having the composition $GeCl_4$, which boils at 86° C. |
| The sulphide will be insoluble in water, but probably soluble in ammonium sulphide. | The sulphide is moderately soluble in water, more readily soluble in ammonium sulphide and the alkalies. |
| The metal will decompose steam very slowly, be scarcely acted on by acids, but easily by alkalies. | Not acted on by hydrochloric acid. Soluble in aqua regia. Nitric acid converts it into the oxide. Sulphuric acid gives the sulphate with liberation of sulphur dioxide. Not acted on by a concentrated solution of potassium hydroxide, but violently by the molten hydroxide. |
| It will form volatile organo-metallic compounds, and will occur in minerals containing titanium and niobium. | Occurs in a silver ore of the composition $3\,Ag_2S, GeS$. |
| According to L. Meyer this element will be: | |
| Easily fusible, | Fuses at 900° C., |
| Volatile, | Easily volatile, |
| Electro-negative, | Probably electro-negative, |
| Brittle. | Very brittle. |

A comparison like this shows that we have here to deal with a case similar to that which presented itself when gallium and scandium were discovered, and shown to be identical with eka-aluminium and eka-boron respectively; and a careful consideration of the results already obtained seems to show that, in all probability, the eka-silicium of Mendelejeff and the germanium discovered by Winkler are the same elements. — (*Journal für prak. Chemie* **34**, 177.) J. H. K.

## *Inosite.*[1]

This substance was first obtained by Scherer from muscular tissue, and has since been found to be a constituent of a large number of plants. The difficulty of obtaining it in any quantity has hitherto prevented its exact study. M. Maquenné has succeeded in obtaining a considerable quantity of it by extracting dried leaves of the walnut tree with water, and has subjected it to careful investigation. He finds that it has the composition represented by the formula $C_6H_{12}O_6 + 2H_2O$; and a determination of its molecular weight by the cryoscopic method of Raoult is also found to be in accord with this formula. It is optically inactive and suffers no change when left in contact with *Penicillium glaucum*. Its molecule, hence, cannot contain an asymmetric carbon atom according to the rule of Le Bel and van't Hoff. Inosite is not attacked by acids nor dilute alkalies. It does not reduce Fehling's solution, nor does it act upon an ammoniacal silver solution. With acid sodium sulphite it does not unite, nor is it reduced by sodium amalgam. The halogens do not act upon it in the cold, but when it is heated with bromine to 100° C. it yields oxidation products similar to those obtained with nitric acid. Inosite is not an aldehyde nor an acetone, since it does not give, on oxidation, an acid containing six atoms of carbon, nor oxy-acids of the fatty series. Its molecule then cannot contain a lateral chain, and it must therefore be a hexatomic alcohol derived from hexahydro-benzene—*i.e.* hexahydro-hexoxy-benzene, $C_6H_6(OH)_6$. The symmetry of this formula excludes, according to the theory of Le Bel and van't Hoff, all rotary power. In another paper,[2] Maquenné shows that, by reduction with hydriodic acid, anhydrous inosite yields a small quantity of benzene and tri-iodophenol—a fact which lends strong support to the formula proposed by him. On oxidising inosite with concentrated nitric acid, he obtained oxy-quinones, such as tetraoxy-quinone, rhodizonic acid, triquinone and croconic acid, all of which have been previously obtained by Nietzki and Benckiser from hexoxy-benzene $C_6(OH)_6$. Hence inosite has the structure represented by the hexagonal symmetrical formula above given, since it yields, both on oxidation and reduction, derivatives of benzene. W. R. O.

[1] Comptes Rendus **104**, 4, 225. [2] *Ibid.* **104**, 5, 297.